nature chemistry

SUPPLEMENTARY INFORMATION

DOI: 10.1038/NCHEM.2686

In the format provided by the authors and unedited.

Atomically precise organomimetic cluster nanomolecules assembled via perfluoroaryl-thiol S_NAr chemistry

*Elaine A. Qian[1,2,4], Alex I. Wixtrom[1], Jonathan C. Axtell[1], Azin Saebi[1], Dahee Jung[1,4], Pavel Rehak[3], Yanxiao Han[3], Elamar Hakim Moully[1], Daniel Mosallaei[1], Sylvia Chow[1], Marco S. Messina[1,4], Jing Yang Wang[1], A. Timothy Royappa[5], Arnold L. Rheingold[6], Heather D. Maynard[1,4], Petr Král[3,7,8] and Alexander M. Spokoyny[1,4]**

[1]Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095, USA.

[2]Department of Bioengineering, University of California, Los Angeles, 410 Westwood Plaza, Los Angeles, California 90095, USA.

[3]Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607, USA.

[4]California NanoSystems Institute, University of California, Los Angeles, 570 Westwood Plaza, Los Angeles, California 90095, USA.

[5]Department of Chemistry, University of West Florida, 11000 University Parkway, Pensacola, Florida 32514, USA.

[6]Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093, USA.

[7]Department of Physics, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607, USA.

[8]Department of Biopharmaceutical Sciences, University of Illinois at Chicago, 833 South Wood Street, Chicago, Illinois 60612, USA.

*Corresponding author:

Alexander M. Spokoyny

Email: spokoyny@chem.ucla.edu

Phone: (+1) 310-357-1327

Table of Contents

General considerations 4

Materials 4

Instruments 5

2D diffusion-ordered (DOSY) ^{1}H NMR spectroscopy 6

High resolution transmission electron microscopy (HRTEM) 6

Size exclusion chromatography-multi angle light scattering (SEC-MALS) 6

Surface plasmon resonance (SPR) 6

X-ray data collection and processing parameters 7

Microwave synthesis 8

Synthesis of **1** 9

Synthesis of **2** 9

Synthesis of 4-pentafluorophenyl(hydroxymethyl) benzene 10

Synthesis of 4-pentafluorophenyl(bromomethyl) benzene 11

Synthesis of **3** 11

Synthesis of **2a** 13

Synthesis of **2b** 14

Synthesis of **2c** 15

Synthesis of **2d** 16

Synthesis of **2e** 17

Synthesis of **2f** 18

Synthesis of **2i** 19

Synthesis of mPEGthiol$_{766}$ [**j**] 20

Synthesis of **2j** 22

Synthesis of **2k** 23

Synthesis of **2l** 24

Synthesis of **3a** 25

Synthesis of **3b** 26

Synthesis of **3c** 27

Synthesis of **3d** 28

Synthesis of **3e** 29

Synthesis of **3f** 30

Synthesis of **3g** 31

Synthesis of **3h** 32

Synthesis of **3i** 33

Synthesis of **3j** 34

Synthesis of **3k** 35

Synthesis of **3l** 36

NMR and mass spectra 38

2D DOSY ^{1}H NMR spectroscopy plots of **2i-k** and **3i-k** 198

Stability studies of **2i** under biologically relevant conditions 204

Plot of conjugation progress of Boc-cysteine (**g**) onto clusters **2**/**3** 222

Computational work 223

References 238

Experimental Section

General considerations. Microwave synthesis reactions and all post-microwave work-up and characterization were performed under ambient conditions. For the purposes of this manuscript, "ambient conditions" refer to room temperature (20 - 28 °C) and uncontrolled laboratory air.

Materials. Deuterated solvents were purchased from Cambridge Isotope Laboratories. MilliQ water described in this manuscript refers to purified potable water with a resistivity at 25 °C of ≤18.2 MΩ·cm. $[NEt_3H]_2[B_{12}H_{12}]$ was purchased from Boron Specialties. EtOH (200 proof) was purchased from Decon Labs. Fmoc-L-amino acids (>98.5%) were purchased from Chem-Impex International, Inc. Piperidine (99%) was purchased from Spectrum. $CaCl_2 \cdot 2\ H_2O$ (≥99%), $MgCl_2 \cdot 6\ H_2O$ (≥99%), $MnCl_2 \cdot 4\ H_2O$ (≥98%), diethyl ether (anhydrous, ≥99.9%), glycine (98%), and Gibco minimum essential medium were purchased from Fisher Scientific. Thiophenol (99%) and poly(ethylene glycol) methyl ether (average MW 750 Da, MW range 715 – 785 Da) were purchased from Acros Organics. HBS-P pH 7.4 buffer (10 mM HEPES, 0.005% v/v Tween P20) and 1 M ethanolamine·HCl (pH 8.5) were purchased from GE Healthcare Life Sciences. Fetal bovine serum was purchased from Sciencell Research Laboratories. $FeCl_3 \cdot 6\ H_2O$ (≥97%), $CsOH \cdot 1\ H_2O$ (≥99.5%), H_2O_2 (30% in H_2O), $[N^nBu_4]OH$ (40% in H_2O), trifluoroacetic acid (TFA, 99%), triisopropylsilane (98%), *N*,*N*-dimethylformamide (DMF, ≥99.8%; anhydrous, 99.8%), MeCN (≥99.9%), CH_2Cl_2 (≥99.5%), ethyl acetate (≥99.5%), hexanes (≥98.5%), MeOH (≥99.8%), *N*,*N*-diisopropylethylamine (≥99%), tetrabutylammonium hexafluorophosphate (≥99.0%, electrochemical grade), 1,2-ethanedithiol (≥98%), 1-hexanethiol (95%), benzyl mercaptan (99%), cysteamine (95%), 2-mercaptoethanol (≥99%), 1-thioglycerol (≥97%), *O*-(2-mercaptoethyl)-*O'*-methyl-hexa(ethylene glycol) (average M_n 356.48 Da, ≥95%), *O*-(2-mercaptoethyl)-*O'*-methylpolyethylene glycol (average M_w 2,000 Da), 1-thio-*β*-D-glucose tetraacetate (97%), *N*-

(*tert*-Butoxycarbonyl)-L-cysteine methyl ester (97%), isopropoxytrimethylsilane (98%), K_3PO_4 (≥98%), K_2CO_3 (≥99%), Tris (≥99%), and triethylamine (≥99%) were purchased from Sigma-Aldrich. All reagents were used as received unless otherwise indicated.

Instruments. Bruker AV300, AV400, AV500, and DRX500 spectrometers were used to obtain ^{1}H, ^{11}B, $^{13}C\{^{1}H\}$, and ^{19}F NMR spectra and Bruker Topspin software was used to process the NMR data. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual solvent resonances in deuterated solvents (due to high humidity, H_2O resonances are often present). ^{11}B and ^{19}F NMR spectra were referenced to $BF_3{\cdot}Et_2O$ and $CFCl_3$ external standards, respectively, at δ 0.0. *in situ* ^{11}B and ^{19}F NMR spectroscopy was run unlocked and unshimmed. ^{11}B NMR spectra were baseline-corrected using the cubic spline correction tool within the Bruker Topspin software. Mass spectrometry data were acquired using a Thermo Scientific Q-Exactive Plus instrument with a quadrupole mass filter and Orbitrap mass analyzer or a Waters LCT Premier TOF system with ACQUITY LC and autosampler. IR spectroscopy was acquired on solid samples using a PerkinElmer Spectrum Two FT-IR spectrometer equipped with a diamond universal ATR probe. High resolution transmission electron microscopy (HRTEM) images were acquired with a FEI Titan electron microscope operating at 300 kV. Size exclusion chromatography-multi angle light scattering (SEC-MALS) was conducted on a GE AKTA PURE chromatographic system equipped with a WYATT miniDawn Treos MALS, WYATT optilab T-rEX RI detector, one Tosoh PWXL guard column (6.0 mm ID x 4.0 cm, 12 μm), and one Tosoh G4000PWxl (7.8 mm ID x 30 cm, 10 μm) column. Surface plasmon resonance (SPR) experiments were run on a GE Healthcare Life Sciences Biacore T100 instrument. Purification of peptides was done using a Waters HPLC system equipped with a UV/Vis detector set at λ = 214 nm.

2D diffusion-ordered (DOSY) ^{1}H NMR spectroscopy. 2D DOSY experiments on purified samples of PEGylated OCNs were performed in D_2O at 30 °C on a Bruker AV 300 spectrometer. The data were processed with the standard Bruker Topspin software – the T1/T2 *vargrad* fitting function was used to determine the diffusion coefficients. 2D DOSY plots were created with the Bruker Topspin software. Hydrodynamic diameters were estimated based on the diffusion coefficients using the Stokes-Einstein Equation.

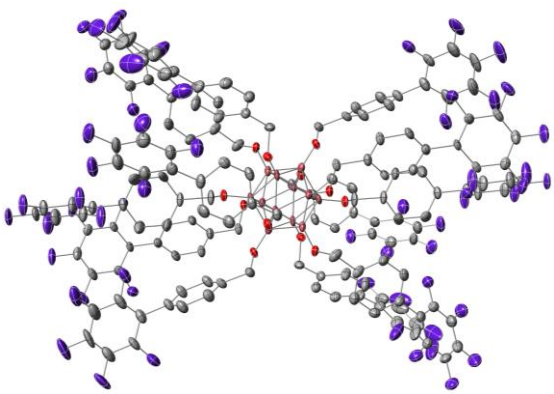
High resolution transmission electron microscopy (HRTEM). HRTEM samples were prepared by dropping 5 μL of 25 μg/mL aqueous sample solutions onto carbon copper grids (Ted Pella). The samples were then blotted once with a filter paper and then left to air-dry for 10 minutes. Then, 3 μL of a 2% w/w uranyl acetate aqueous solution was dropped on the grids, and subsequently blotted after 2 minutes.

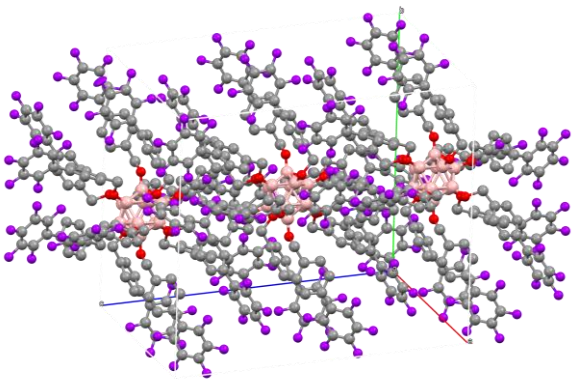
Size exclusion chromatography-multi angle light scattering (SEC-MALS). Samples for SEC-MALS were prepared by dissolving sample in MilliQ water and filtering sample through a 0.20 μm PTFE Fisherbrand syringe filter. Eluent was Millipore filtered MilliQ water with 0.02% NaN_3 at 12 °C (flow rate: 0.70 mL/min). Chromatograms were analyzed using Astra 6.0 software.

Surface plasmon resonance (SPR). All experiments were performed on a Biacore T100 instrument with a Series S CM5 chip (GE Healthcare Life Sciences). The procedure used here was modified from a published procedure by Safina *et al.*[1] The running buffer was 10 mM HEPES buffer (pH 7.4) with 0.005% Tween P20, 1 mM $CaCl_2$, 1 mM $MgCl_2$, and 1 mM $MnCl_2$. 5 μL/min flow rate was used throughout the experiments. First, a reference channel (flow cell 1) was prepared by activating the surface with a 0.4 M EDC and 0.1 M NHS (1:1 v/v) mixture during 30 minutes, then 1 M ethanolamine HCl (pH 8.5) during 40 minutes. Then, the sample channel (flow cell 2) was activated using under the EDC/NHS conditions, followed by injection of 0.1 mg/mL

ConA for 40 minutes and then 1 M ethanolamine HCl for 30 minutes for blocking. Analyte samples of 0.022 μM to 130 μM were injected in tandem over both cells for 6 minutes. Surfaces were regenerated by injecting 10 mM HCl for 2 minutes followed by injecting 10 mM glycine HCl (pH 2.5) for 2 minutes. Binding curves at various analyte concentrations were fitted to the Langmuir 1:1 binding model for an estimation of the binding constants. For the purpose of figure presentation, the sensorgrams were processed using the smoothing function in the OriginPro data analysis software.

X-ray data collection and processing parameters. For **2**, a single crystal was mounted on a nylon loop using perfluoropolyether oil and cooled rapidly to 100 K with a stream of cold dinitrogen. Diffraction data were measured using a Bruker APEX-II CCD diffractometer using Mo-K_α radiation. The cell refinement and data reduction were carried out using Bruker SAINT and the structure was solved with SHELXS-97. All subsequent crystallographic calculations were performed using SHELXL-2013. For **3**, single-crystal diffraction data were collected at 100(2) K on a Bruker Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). After correcting for absorption and polarization effects, structure solution and refinement were carried out using the SHELXT[2], XL[3] and Olex2[4] software suites. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters, and hydrogen atoms were placed in suitable riding positions.



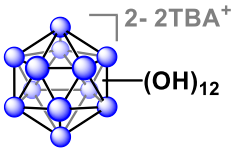


3

compound		**3**
empirical formula		$C_{78}H_{36}B_6F_{30}O_6$
fw		1703.95
temp / K		100
wavelength / Å		0.71073 Å
space group		*P* -1
a / Å		19.211(3)
b / Å		19.674(3)
c / Å		22.866(4)
α / deg		97.606(5)
β / deg		114.089(5)
γ / deg		109.756(5)
V / Å		7047.9(18)
Z		2
d (calcd) / $Mg \cdot m^{-3}$		1.606
abs coeff / mm^{-1}		0.153
R indices:	R_1 =	0.1771
	R_w =	0.2030

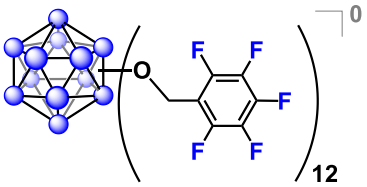
Microwave synthesis. Microwave reactions were performed using a CEM Discover SP microwave synthesis reactor. Except where noted otherwise, all reactions were performed in glass 10 mL microwave reactor vials purchased from CEM with silicone/PTFE caps. Flea micro PTFE-coated stir bars (10 mm x 3 mm) were used in the vials with magnetic stirring set to high and 15 seconds of premixing prior to the temperature ramping. All microwave reactions were carried out at 140 °C with the pressure release limit set to 250 psi (no reactions exceeded this limit to trigger venting) and the maximum wattage set to 250 W (the power applied was dynamically controlled by the microwave instrument and did not exceed this limit for any reactions). Column chromatography was performed using 2.0 - 2.25 cm inner diameter glass fritted chromatography columns with 20-30 cm of slurry-packed silica gel to ensure full separation of reagents and products. Unfiltered pressurized air was used to assist column chromatography.

Synthesis of 1



The $[N^nBu_4]_2$ salt of $[B_{12}(OH)_{12}]^{2-}$ was prepared according to the procedures detailed in Wixtrom *et al.* 2016.[5] *From this point, N^nBu_4 will be referred to as TBA. Note:* ***1*** *is air-stable, but hygroscopic. Store under inert atmosphere or in a sealed desiccator to prevent excess absorption of water over extended periods of time in storage.*

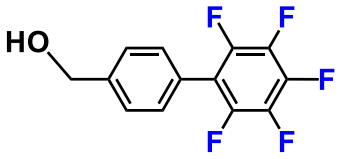
Synthesis of 2



Previously reported protocol[6] used to synthesize compound **2** – procedure is duplicated here. Compound **1** (300 mg, 0.366 mmol) was transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 4 mL acetonitrile in a 30 mL glass microwave vial. *N*,*N*-diisopropylethylamine (1.21 mL, 6.96 mmol) and 2,3,4,5,6-pentafluorobenzyl bromide (6.86 mL 45.4 mmol) were added along with a magnetic stir bar, the vial was sealed with a Teflon/silicone cap, and the reaction mixture was heated under microwave conditions at 140˚C with high stirring for 15 minutes. The volatiles were removed via rotary evaporation, and the excess reagent was eluted through a silica column with 65/35 hexanes/ethyl acetate, and the pink/purple product mixture was eluted with acetone. The acetone was removed via rotary evaporation and the residue was dissolved in ~5 mL 90/5/5 ethanol/acetonitrile/H_2O. $FeCl_3 \cdot 6H_2O$ (1.88 g, 6.96 mmol) was added and the mixture was left to stir for 24 hours. The mixture was concentrated *in vacuo*. The

residue (while still in the round bottom flask) was rinsed three times with water. The residue was then taken up in toluene and extracted three times with water. The organic fractions were combined and dried under vacuum. The resulting solid was charged with hexane and isolated by filtration to afford an orange/yellow solid (574 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.23 (s, 24H). ^{11}B NMR (160 MHz, $CDCl_3$): δ 40.9. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 60.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -145.1 (d, 24F, -*ortho*), -152.2 (t, 12F, -*para*), -161.3 – -161.5 (m, 24F, -*meta*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{84}H_{84}B_{12}O_{12}$ (M^-), 2494.1499 Da; found, 2494.1631 Da. Crystallized from $CDCl_3$ at room temperature for 1 week to obtain a single crystal for X-ray diffraction analysis.

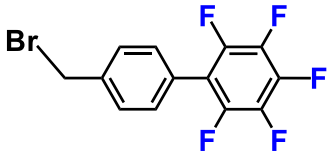
Synthesis of 4-pentafluorophenyl(hydroxymethyl) benzene



A solution of 4-pentafluorophenyl benzaldehyde (0.900 g, 3.30 mmol) and sodium borohydride (0.150 g, 3.96 mmol) in 14 mL tetrahydrofuran and 7 mL ethanol was prepared and placed under a positive nitrogen flow. The mixture was stirred at room temperature for 24 hours. The resulting dark solution was diluted with water (30 mL) and extracted with methylene chloride (30 mL). The organic layer was washed three times with H_2O, dried over $MgSO_4$, and filtered through Celite. The solvent was then dried *in vacuo*. The residue was purified by flash chromatography (eluent: DCM; R_f = 0.4) through a silica column, using UV light for TLC visualization. The resulting solution was dried under vacuum, providing 4-pentafluorophenyl(hydroxymethyl) benzene as a white solid (0.705 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, 2H, Ar), 7.42 (d, 2H, Ar), 4.76 (d, 2H, CH_2OH), 2.05 (t, 1H, CH_2OH). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 144.3, 142.3, 140.6,

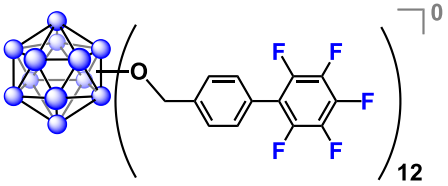
138.1, 130.5, 127.2, 126.3, 115.8, 64.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -143.3 (q, 2F, -*ortho*), -155.5 (t, 1F, -*para*), -162.2 (m, 2F, -*meta*).

Synthesis of 4-pentafluorophenyl(bromomethyl) benzene



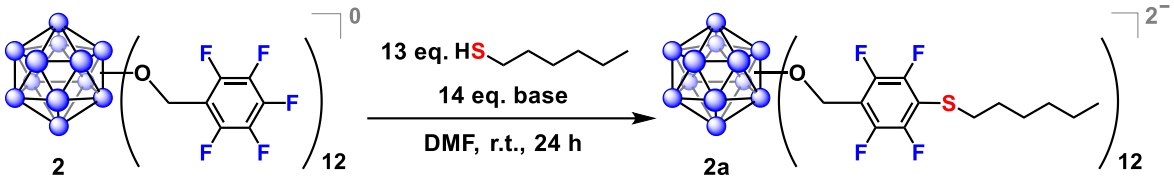
A flask containing 4-pentafluorophenyl(hydroxymethyl) benzene (1.00 g, 3.65 mmol) was purged with nitrogen and 30 mL of dry methylene chloride was charged into the flask. The solution was placed in ice bath and PBr_3 (346 μL, 3.65 mmol) was added *via* syringe. The reaction mixture was stirred overnight, during which time the mixture turned yellow. The resulting mixture was then diluted with 100 mL distilled H_2O. The organic layer was separated and washed 3 times with saturated NaCl solution. Organic layer was collected and dried over $MgSO_4$, then filtered through Celite. Solvent was evaporated and the residue was purified by flash chromatography (hexane/CH_2Cl_2, 2:1; R_f = 0.75) through a silica column, using UV light for TLC visualization. The resulting solution was dried under vacuum, providing 4-pentafluorophenyl(bromomethyl) benzene as a white solid (0.773 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, 2H, Ar), 7.42 (d, 2H, Ar), 4.54 (s, 2H, CH_2Br). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 144.3, 140.7, 139.1, 138.0, 130.7, 129.5, 126.6, 115.4, 32.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -143.1 (q, 2F, -*ortho*), -155.1 (t, 1F, -*para*), -162.0 (m, 2F, -*meta*).

Synthesis of 3



Compound **1** (75.0 mg, 0.092 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen-filled glovebox, opened to the air, and dissolved in 1.5 mL acetonitrile. *N,N*-diisopropylethylamine (0.3 mL, 1.73 mmol) and 4-pentafluorophenyl(bromomethyl) benzene (0.8334 g, 2.47 mmol) were added along with a flea micro stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 30 minutes. The volatiles were removed *via* rotary evaporation, and the remaining reagent was eluted first through a slurry-packed silica gel column with 80/20 hexanes/CH_2Cl_2, and the pink/purple product mixture was eluted with acetone followed by CH_2Cl_2. *Note: The eluted fraction containing the reagent ligand can be purified by eluting through a silica column with 90/10 hexanes/CH_2Cl_2, and after drying thoroughly it can be used for subsequent synthesis of **3**. Recycling the ligand in this manner can minimize unnecessary repetition of ligand synthesis.* The volatiles were removed *via* rotary evaporation, and the remaining charged 2-/1- product mixture was dissolved in 5 mL 90/10 EtOH/MeCN. $FeCl_3 \cdot 6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 24 hours. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and a red-orange band containing the neutral product was separated from the $FeCl_3 \cdot 6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final neutral product **2** was dried under high vacuum to obtain an isolated yield of 266.5 mg (85%). Compound **2** is a dark red-orange solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.21 - 7.33 (m, 48H, $C_6\underline{H}_4$), 5.50 (s, 24H, $OC\underline{H}_2$). $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2): δ 42.4. ^{19}F NMR (376 MHz, CD_2Cl_2): δ -144.2 (q, 24F, -*ortho*), -156.5 (t, 12F, -*para*), -163.4 – -163.5 (m, 24F, -*meta*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{165}H_{72}B_{12}F_{60}O_{12}$ (M^-), 3407.5289 Da; found, 3407.5278 Da. X-ray quality crystals of **3** were grown from a cooling solution of boiling 1:1 EtOH:MeOH.

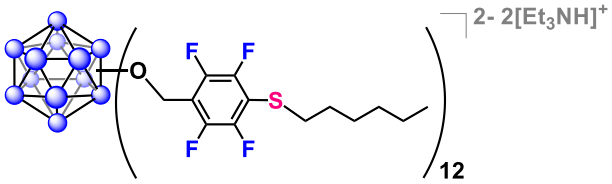
Supplementary Table 1. Initial Studies and Reaction Optimization



Entry	Base	Yield[a] (%)
1	NEt_3	3
2	Tris	7
3	K_3PO_4	72
4	K_2CO_3	87

[a]Yield determined by ^{19}F NMR. Tris, tris(hydroxymethyl)aminomethane.

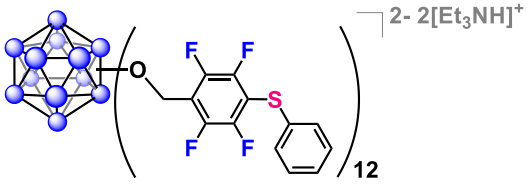
Synthesis of 2a



2 (5.0 mg, 0.0020 mmol) and K_2CO_3 (8.4 mg, 0.061 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by 1-hexanethiol (3.76 μL, 0.027 mmol). The vial was sealed again and set to stir at 400 rpm for 22 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾" glass Pasteur

pipet column was prepared using glass wool and 4" of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing **2a** was loaded onto the column with 80/20 hexanes/ethyl acetate (sonication was used to aid dissolution), and the remaining reagent was eluted with 80/20 hexanes/ethyl acetate. A very slightly yellow band containing **2a** was eluted with MeCN, and the fractions containing **2a** (as assessed by TLC) were combined and volatiles were removed *via* rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 5.4 mg (70%). ^{1}H NMR (400 MHz, CD_3CN): δ 5.42 (br s, 24H, $OC\underline{H}_2$), 3.12 (q, 12H, $[(CH_3C\underline{H}_2)_3NH]^+$), 2.89 – 2.82 (m, 24H, $SC\underline{H}_2$), 1.49 - 1.39 (m, 24H, $SCH_2C\underline{H}_2$), 1.36 – 1.26 (br m, 24H, $S(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.24 (t, 18H, $[(C\underline{H}_3CH_2)_3NH]^+$), 1.21 – 1.10 (br m, 48H, $S(CH_2)_2(C\underline{H}_2)_3CH_3$), 0.83 – 0.74 (m, 36H, $S(CH_2)_5C\underline{H}_3$). ^{11}B{^{1}H} NMR (128 MHz, CD_3CN): δ -15.8. ^{19}F NMR (376 MHz, CD_3CN): δ -137.4 (br m, 24F, -*meta*[7]), -145.1 (br m, 24F, -*ortho*[7]). MS (LCT Premier): *m/z* calculated for $C_{156}H_{180}B_{12}F_{48}O_{12}S_{12}$ (M^{2-}), 1836.52 Da; found, 1836.29 Da.

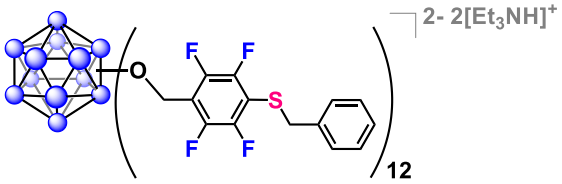
Synthesis of 2b



2 (5.0 mg, 0.0020 mmol) and K_3PO_4 (9 mg, 0.042 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by thiophenol (2.66 μL, 0.026 mmol). The vial was sealed again and set to stir at 400 rpm for 25 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR

tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾" glass Pasteur pipet column was prepared using glass wool and 4" of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing **2b** was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing **2b** was eluted with MeCN, and the fractions containing **2b** (as assessed by TLC) were combined and volatiles were removed *via* rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 6.8 mg (90%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.22 – 7.14 (br m, 60H, S-Ar), 5.49 (br s, 24H, OCH_2), 3.11 (q, 12H, $[(CH_3CH_2)_3NH]^+$), 1.23 (t, 18H, $[(CH_3CH_2)_3NH]^+$). ^{11}B{^{1}H} NMR (128 MHz, CD_3CN): δ -15.7. ^{19}F NMR (376 MHz, CD_3CN): δ -136.4 (m, 24F, -*meta*), -144.1 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{156}H_{84}B_{12}F_{48}O_{12}S_{12}$ (M^{2-}), 1788.1481 Da; found, 1788.1514 Da.

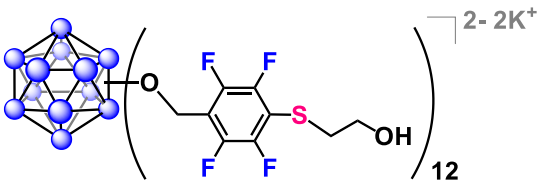
Synthesis of 2c



2 (5.0 mg, 0.0020 mmol) and K_3PO_4 (8.1 mg, 0.038 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by benzyl mercaptan (3.53 μL, 0.030 mmol). The vial was sealed again and set to stir at

400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾" glass Pasteur pipet column was prepared using glass wool and 4" of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing **2c** was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing **2c** was eluted with MeCN, and the fractions containing **2c** (as assessed by TLC) were combined and volatiles were removed *via* rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 7.4 mg (93.5%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.20 – 7.04 (br m, 60H, SCH_2-Ar), 5.39 (br s, 24H, OCH_2), 4.05 (m, 24H, SCH_2), 3.11 (q, 12H, $[(CH_3CH_2)_3NH]^+$), 1.23 (t, 18H, $[(CH_3CH_2)_3NH]^+$). ^{11}B{^{1}H} NMR (128 MHz, CD_3CN): δ -15.8. ^{19}F NMR (376 MHz, CD_3CN): δ -136.8 (m, 24F, -*meta*), -144.8 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{168}H_{108}B_{12}F_{48}O_{12}S_{12}$ (M^{2-}), 1872.2420 Da; found, 1872.2469 Da.

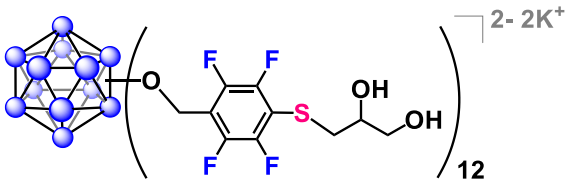
Synthesis of 2d



2 (5.0 mg, 0.0020 mmol) and K_3PO_4 (10.4 mg, 0.049 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred

into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by 2-mercaptoethanol (2.26 μL, 0.032 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing **2d** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 2.6 mg (40 %). ^{1}H NMR (400 MHz, CD_3OD): δ 5.50 (br s, 24H, $OC\underline{H_2}$), 3.64 (t, 24H, $CH_2C\underline{H_2}OH$), 3.00 (t, $SC\underline{H_2}CH_2$). ^{11}B NMR (128 MHz, CD_3OD): δ -15.7. ^{19}F NMR (376 MHz, CD_3OD): δ -137.6 – -137.7 (m, 24F, -*meta*), -145.1 – -145.2 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{108}H_{84}B_{12}F_{48}O_{24}S_{12}$ (M^{2-}), 1596.1176 Da; found, 1596.1233 Da.

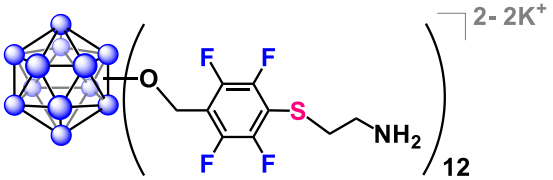
Synthesis of 2e



2 (5.0 mg, 0.0020 mmol) and K_3PO_4 (10.2 mg, 0.048 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added,

followed by thioglycerol (3.12 μL, 0.036 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing **2e** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 2.2 mg (30 %). ^{1}H NMR (400 MHz, CD_3OD): δ 5.50 (br s, 24H, OCH_2), 3.69 – 3.64 (m, 12H, $SCH_2CH(OH)$), 3.60 – 3.53 (m, 24H, $CH(OH)CH_2OH$), 3.07 – 2.93 (m, 24H, $SCH_2CH(OH)$). ^{11}B NMR (128 MHz, CD_3OD): δ -15.6. ^{19}F NMR (376 MHz, CD_3OD): δ -137.5 – -137.6 (m, 24F, -*meta*), -145.1 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{120}H_{108}B_{12}F_{48}O_{36}S_{12}$ (M^{2-}), 1776.1810 Da; found, 1776.1894 Da.

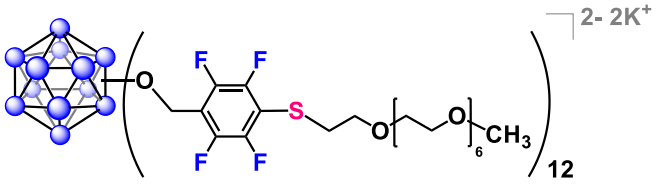
Synthesis of 2f



2 (5.0 mg, 0.0020 mmol) and K_2CO_3 (2.6 mg, 0.019 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added,

followed by cysteamine (3.7 mg, 0.048 mmol). The vial was sealed again and set to stir at 400 rpm for 23 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in 40/60 MeOH/MeCN (23 cm packed height), and the crude product mixture containing **2f** was loaded onto the column with 40/60 MeOH/MeCN. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 3.2 mg (49 %). ^{1}H NMR (400 MHz, CD_3OD): δ 5.51 (br s, 24H, $OC\underline{H_2}$), 2.94 (t, 24H, $SC\underline{H_2}CH_2$), 2.72 (t, $CH_2C\underline{H_2}NH_2$). ^{11}B NMR (128 MHz, CD_3OD): δ -15.4. ^{19}F NMR (376 MHz, CD_3OD): δ -137.6 (m, 24F, -*meta*), -144.4 – -144.6 (m, 24F, -*ortho*). MS (LCT Premier): *m/z* calculated for $C_{108}H_{96}B_{12}F_{48}N_{12}O_{12}S_{12}$ (M^{2-}), 1590.21 Da; found, 1590.07 Da.

Synthesis of 2i

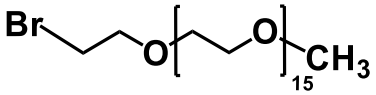


2 (8 mg, 0.0032 mmol) and K_3PO_4 (16.6 mg, 0.078 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 240 μL anhydrous DMF was added, followed by $mPEGthiol_{356}$ (20.63 μL, 0.064 mmol). The vial was sealed again and set to stir at 400 rpm for

28 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing **2i** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 16.9 mg (81 %). ^{1}H NMR (400 MHz, CD_3OD): δ 5.51 (br s, 24H, $OC\underline{H}_2$), 3.63 – 3.50 (m, 312H, $SCH_2C\underline{H}_2O(C\underline{H}_2C\underline{H}_2O)_6$), 3.35 – 3.33 (m, 36H, $(CH_2CH_2O)_6C\underline{H}_3$), 3.08 (t, 24H, $SC\underline{H}_2$). ^{11}B NMR (128 MHz, CD_3OD): δ -15.7. ^{19}F NMR (376 MHz, CD_3OD): δ -137.2 – -137.3 (m, 24F, -*meta*), -144.8 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{264}H_{396}B_{12}F_{48}O_{96}S_{12}$ (M^{2-}), 3265.1552 Da; found, 3265.1444 Da.

Synthesis of j

1. Synthesis of j-Br

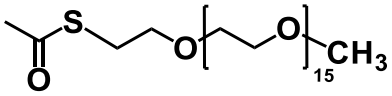


In a round bottom flask, $mPEG_{750}$ (7.50 g, 10.00 mmol) and CBr_4 (3.98 g, 12.00 mmol) were dissolved in 40 mL of acetonitrile. To the stirring solution, PPh_3 (3.15 g, 6.00 mmol) was added in small portions over 30 minutes. The mixture was then left stirring at room temperature for 4 hours. After 4 hours, the solvent was then removed *in vacuo* and the resulting yellow-orange oil was dissolved in 20 mL of H_2O and left at 4 °C overnight, producing a white precipitate. The mixture was filtered through Celite* on a glass frit and the filtrate was washed twice with 5 mL of

toluene. The aqueous layer was dried *in vacuo* to yield the desired product as an orange oil (7.08 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.55 – 3.51 (m, 62H, $C\underline{H_2}O(C\underline{H_2}C\underline{H_2}O)_{15}$), 3.43 (m, 2H, $BrC\underline{H_2}$), 3.26 (s, 3H, $(CH_2CH_2O)_{15}C\underline{H_3}$).

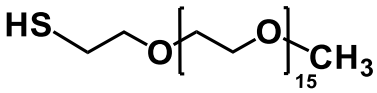
*Celite was pretreated on the frit by washing with 30 mL of H_2O before the mixture was filtered.

2. Synthesis of j-SAc



To a solution of **j-Br** (1.07 g, 1.32 mmol) in 35 mL of ethanol, potassium thioacetate (0.20 g, 1.75 mmol) was added in one portion. The mixture was refluxed at 120 °C for 5 hours. The resulting suspension was filtered through Celite and the filtrate was dried under vacuum, affording a brown oil. The oil was dissolved in 40 mL of chloroform and the organic phase was washed twice with H_2O. The organic layer was dried over Na_2SO_4 and filtered through Celite. The solvent was removed *in vacuo*, providing **j-SAc** (0.64 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 – 3.61 (m, 62H, $C\underline{H_2}O(C\underline{H_2}C\underline{H_2}O)_{15}$), 3.36 (s, 3H, $(CH_2CH_2O)_{15}C\underline{H_3}$), 3.07 (t, 2H, $SC\underline{H_2}$), 2.32 (s, 3H, $SCOC\underline{H_3}$).

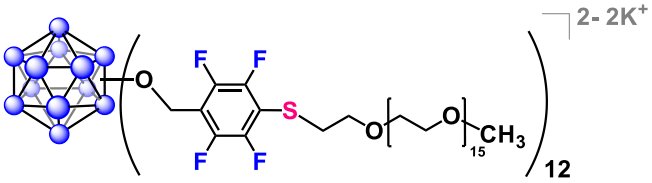
3. Synthesis of j



j-SAc (405 mg, 0.5 mmol) was charged with 5 mL of 1M HCl and was refluxed at 110 °C for 2 hours under a blanket of Ar. The solvent was removed *in vacuo*. The residue was dissolved in 10 mL of DCM and the organic phase was washed twice with water. The organic layer was separated and dried over Na_2SO_4 and filtered through Celite. The solution was dried under vacuum to yield the desired product as a brown oil (319 mg, 83%). Product was stored under inert atmosphere. ^{1}H

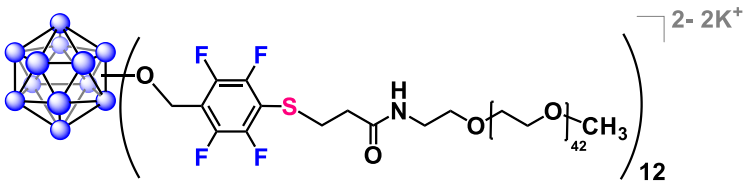
NMR (400 MHz, CD_2Cl_2): δ 3.58 – 3.59 (m, 62H, $C\underline{H_2}O(C\underline{H_2}C\underline{H_2}O)_{15}$), 3.32 (s, 3H, $(CH_2CH_2O)_{15}C\underline{H_3}$), 2.67 (dt, 2H, $SHC\underline{H_2}$), 1.61 (t, 1H, $S\underline{H}CH_2$).

Synthesis of 2j



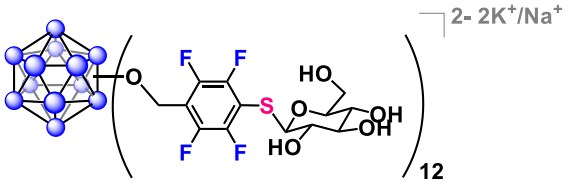
2 (5.0 mg, 0.0020 mmol) and K_3PO_4 (19.2 mg, 0.090 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by $mPEGthiol_{766}$ (48.1 μL, 0.069 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing **2j** was loaded onto the column with water. 15 1-2 mL fractions were collected, dried *via* lyophilization, and subjected to characterization *via* ^1H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* lyophilization to obtain an isolated yield of 4.4 mg (19 %). ^1H NMR (400 MHz, CD_3OD): δ 5.50 (br s, 24H, $OC\underline{H_2}$), 3.63 – 3.53 (m, 744H, $SCH_2C\underline{H_2}O(C\underline{H_2}C\underline{H_2}O)_{15}$), 3.35 (m, 36H, $(CH_2CH_2O)_{15}C\underline{H_3}$), 3.08 (t, 24H, $SC\underline{H_2}$). ^{11}B NMR (128 MHz, CD_3OD): δ -16.0. ^{19}F NMR (376 MHz, CD_3OD): δ -137.2 (m, 24F, -*meta*), -144.8 (m, 24F, -*ortho*).

Synthesis of 2k



2 (5.0 mg, 0.0020 mmol) and K_3PO_4 (13.4 mg, 0.063 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by mPEGthiol$_{2000}$ (101.0 mg, 0.051 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing **2k** was loaded onto the column with water. 15 1-2 mL fractions were collected, dried *via* lyophilization, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* lyophilization to obtain an isolated yield of 21.5 mg (41 %). ^{1}H NMR (400 MHz, CD_3OD): δ 5.50 (br s, 24H, $OC\underline{H_2}$), 3.82 – 3.45 (m, 2100H, $SC\underline{H_2}CH_2(CON\underline{H})C\underline{H_2}C\underline{H_2}O(C\underline{H_2}C\underline{H_2}O)_{42}$), 3.36 (s, 36H, $(CH_2CH_2O)_{42}C\underline{H_3}$), 3.09 (t, 24H, $SCH_2C\underline{H_2}$). ^{11}B NMR (128 MHz, CD_3OD): δ -16.0. ^{19}F NMR (376 MHz, CD_3OD): δ -137.0 – -137.1 (m, 24F, -*meta*), -144.8 (m, 24F, -*ortho*). GPC trace of **2k** measured in water with 0.02% NaN_3 at 12 °C gives a Đ (polydispersity index) of 1.003 (see Fig. 3c in main text).

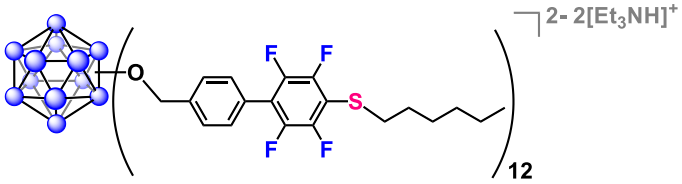
Synthesis of 2l



2 (5.0 mg, 0.0020 mmol) and K_3PO_4 (13.0 mg, 0.061 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by 1-thio-*β*-D-glucose tetraacetate (25.0 mg, 0.069 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. The resulting residue was treated with NaOMe (6.0 mg, 0.11 mmol) in 1 mL MeOH for 2 hours. The volatiles were removed *via* rotary evaporation. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing **2l** was loaded onto the column with water. 15 1-2 mL fractions were collected, dried *via* lyophilization, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* lyophilization to obtain an isolated yield of 1.6 mg (17 %). ^{1}H NMR (400 MHz, D_2O): δ 5.64 – 5.45 (br s, 24H, $OC\underline{H}_2$), 4.03 – 3.20 (m, 84H, $SC\underline{H}C\underline{H}_2OH(C\underline{H}OH)_3C\underline{H}O$). ^{11}B NMR (128 MHz, D_2O): δ -16.3. ^{19}F NMR (376 MHz, D_2O): δ -134.3 – -135.6 (m, 24F, -*meta*), -143.5 (m, 24F, -

ortho). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{156}H_{156}B_{12}F_{48}O_{72}S_{12}$ (M^{2-}), 2304.2772 Da; found, 2304.2769 Da.

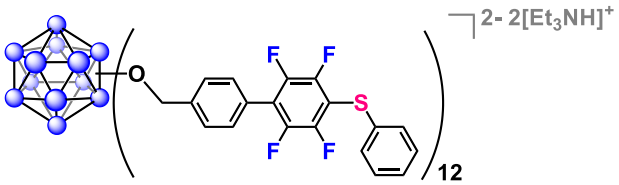
Synthesis of 3a



3 (10.0 mg, 0.0029 mmol) and K_2CO_3 (22.0 mg, 0.159 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by 1-hexanethiol (5.42 μL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 7 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾" glass Pasteur pipet column was prepared using glass wool and 4" of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing **3a** was loaded onto the column with 80/20 hexanes/ethyl acetate (sonication was used to aid dissolution), and the remaining reagent was eluted with 80/20 hexanes/ethyl acetate. A very slightly yellow band containing **3a** was eluted with MeCN, and the fractions containing **3a** (as assessed by TLC) were combined and volatiles were removed *via* rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 12.2 mg (87%). ^1H NMR (400 MHz, CD_3CN): δ 7.64 – 7.50 (br m, 24H, OCH_2-Ar), 7.25 – 7.15 (br m, 24H, OCH_2-Ar), 5.60 (br s, 24H, OCH_2), 3.06 (q, 12H,

[($CH_3C\underline{H}_2)_3NH]^+$), 2.93 (t, 24H, $SC\underline{H}_2$), 1.61 - 1.49 (m, 24H, $SCH_2C\underline{H}_2$), 1.44 – 1.34 (br m, 24H, $S(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.30 – 1.21 (br m, 48H, $S(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.18 (t, 18H, $[(C\underline{H}_3CH_2)_3NH]^+$), 0.89 – 0.80 (m, 36H, $S(CH_2)_5C\underline{H}_3$). $^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ -15.1. ^{19}F NMR (376 MHz, CD_3CN): δ -136.7 (q, 24F, -*meta*), -145.2 (q, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{228}H_{228}B_{12}F_{48}O_{12}S_{12}$ (M^{2-}), 2292.7115 Da; found, 2292.7157 Da.

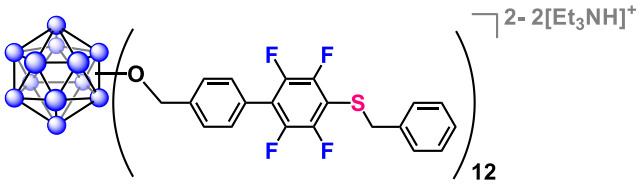
Synthesis of 3b



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (18.9 mg, 0.089 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by thiophenol (3.89 μL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 7 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾" glass Pasteur pipet column was prepared using glass wool and 4" of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing **3b** was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing **3b** was eluted with MeCN, and the fractions containing **3b** (as assessed by TLC) were

combined and volatiles were removed *via* rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 11.7 mg (85%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.65 – 7.48 (br m, 24H, OCH_2-Ar), 7.34 – 7.20 (br m, 60H and 24H, S-Ar and OCH_2-Ar), 5.61 (br s, 24H, OCH_2), 3.09 (q, 12H, $[(CH_3CH_2)_3NH]^+$), 1.21 (t, 18H, $[(CH_3CH_2)_3NH]^+$). ^{11}B{^{1}H} NMR (128 MHz, CD_3CN): δ -15.1. ^{19}F NMR (376 MHz, CD_3CN): δ -135.9 (m, 24F, -*meta*), -145.2 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{228}H_{132}B_{12}F_{48}O_{12}S_{12}$ (M^{2-}), 2244.3359 Da; found, 2244.3381 Da.

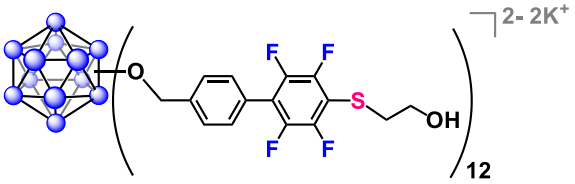
Synthesis of 3c



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (22.5 mg, 0.106 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by benzyl mercaptan (4.48 μL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 5 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾" glass Pasteur pipet column was prepared using glass wool and 4" of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing **3c** was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the

remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing **3c** was eluted with MeCN, and the fractions containing **3c** (as assessed by TLC) were combined and volatiles were removed *via* rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 11.6 mg (81%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.59 – 7.52 (br d, 24H, OCH_2-Ar), 7.26 – 7.15 (br m, 60H and 24H, SCH_2-Ar and OCH_2-Ar), 5.60 (br s, 24H, OCH_2), 4.11 (br s, 24H, SCH_2), 3.06 (q, 12H, $[(CH_3CH_2)_3NH]^+$), 1.18 (t, 18H, $[(CH_3CH_2)_3NH]^+$). ^{11}B{^{1}H} NMR (128 MHz, CD_3CN): δ -15.1. ^{19}F NMR (376 MHz, CD_3CN): δ -135.9 (q, 24F, -*meta*), -145.1 (q, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{240}H_{156}B_{12}F_{48}O_{12}S_{12}$ (M^{2-}), 2328.9298 Da; found, 2328.9363 Da.

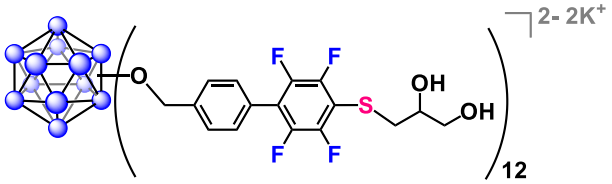
Synthesis of 3d



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (12.3 mg, 0.058 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by 2-mercaptoethanol (2.69 μL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed

height), and the crude product mixture containing **3d** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 10.0 mg (81 %). ^{1}H NMR (400 MHz, CD_3OD): δ 7.61 – 7.45 (br m, 24H, OCH_2-Ar), 7.24 – 7.13 (br m, 24H, OCH_2-Ar), 5.65 (br m, 24H, OCH_2), 3.73 (t, 24H, CH_2CH_2OH), 3.10 (t, SCH_2CH_2). ^{11}B NMR (128 MHz, CD_3OD): δ -15.1. ^{19}F NMR (376 MHz, CD_3OD): δ -136.8 – -136.9 (m, 24F, -*meta*), -145.4 – -145.5 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{180}H_{132}B_{12}F_{48}O_{24}S_{12}$ (M^{2-}), 2052.3054 Da; found, 2052.3080 Da.

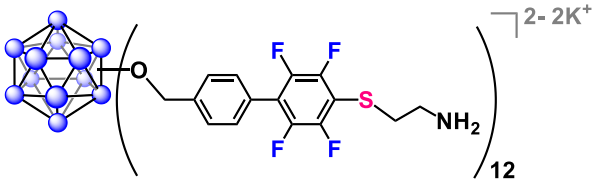
Synthesis of 3e



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (13.1 mg, 0.062 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by thioglycerol (3.30 μL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the

crude product mixture containing **3e** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 7.9 mg (59 %). ^{1}H NMR (400 MHz, CD_3OD): δ 7.59 – 7.45 (br m, 24H, OCH_2-Ar), 7.23 – 7.16 (br m, 24H, OCH_2-Ar), 5.64 – 5.60 (br m, 24H, OCH_2), 3.78 – 3.72 (m, 12H, $SCH_2CH(OH)$), 3.65 – 3.57 (m, 24H, $CH(OH)CH_2OH$), 3.17 – 3.02 (m, 24H, $SCH_2CH(OH)$). ^{11}B NMR (128 MHz, CD_3OD): δ -15.1. ^{19}F NMR (376 MHz, CD_3OD): δ -136.6 – -136.7 (m, 24F, -*meta*), -145.5 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{192}H_{156}B_{12}F_{48}O_{36}S_{12}$ (M^{2-}), 2232.3688 Da; found, 2232.3752 Da.

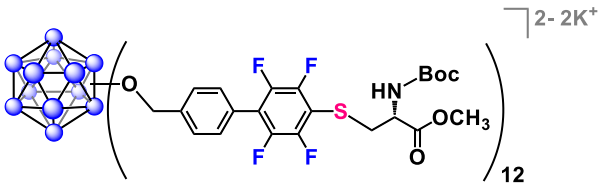
Synthesis of 3f



3 (10.0 mg, 0.0029 mmol) and K_2CO_3 (8.1 mg, 0.059 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by cysteamine (4.9 mg, 0.064 mmol). The vial was sealed again and set to stir at 400 rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in 40/60 MeOH/MeCN (23 cm packed height),

and the crude product mixture containing **3f** was loaded onto the column with 40/60 MeOH/MeCN. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 4.0 mg (33 %). ^{1}H NMR (400 MHz, 33/67 CD_3OD/CD_3CN): δ 7.55 – 7.52 (br m, 24H, OCH_2-Ar), 7.21 – 7.18 (br m, 24H, OCH_2-Ar), 5.60 – 5.54 (br m, 24H, OCH_2), 2.95 (t, 24H, SCH_2CH_2), 2.70 (t, $CH_2CH_2NH_2$). ^{11}B NMR (128 MHz, 33/67 CD_3OD/CD_3CN): δ -15.2. ^{19}F NMR (376 MHz, 33/67 CD_3OD/CD_3CN): δ -136.0 – -136.5 (m, 24F, -*meta*), -145.1 – -145.6 (m, 24F, -*ortho*). MS (LCT Premier): *m/z* calculated for $C_{180}H_{144}B_{12}F_{48}N_{12}O_{12}S_{12}$ (M^{2-}), 2046.40 Da; found, 2046.31 Da.

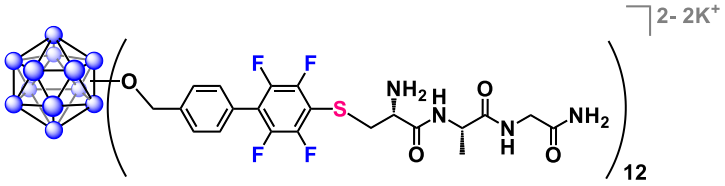
Synthesis of 3g



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (18.7 mg, 0.088 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by *N*-(*tert*-Butoxycarbonyl)-L-cysteine methyl ester (8.16 μL, 0.040 mmol). The vial was sealed again and set to stir at 400 rpm for 3 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for

solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing **3g** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 8.8 mg (49 %). ^{1}H NMR (400 MHz, CD_3OD): δ 7.52 (d, 24H, OCH_2-Ar), 7.19 (d, 24H, OCH_2-Ar), 5.63 (br s, 24H, OCH_2), 4.37 – 4.34 (br m, 12H, SCH_2CH), 3.69 (m, 36H, OCH_3), 3.49 – 3.44 (br m, 24H, SCH_2), 1.35 – 1.33 (m, 108H, $C(CH_3)_3$). ^{11}B NMR (128 MHz, CD_3OD): δ -15.1. ^{19}F NMR (376 MHz, CD_3OD): δ -135.9 – -136.0 (m, 24F, -*meta*), -144.8 – -145.1 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{264}H_{264}B_{12}F_{48}N_{12}O_{60}S_{12}$ (M^{2-}), 2994.7487 Da; found, 2994.7404 Da.

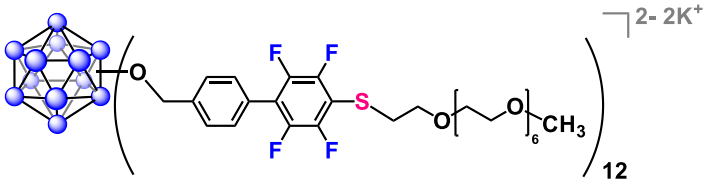
Synthesis of 3h



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (56.1 mg, 0.264 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by unprotected C-A-G·TFA (synthesized using conventional Fmoc solid-phase peptide synthesis protocol[8]) (17.8 mg, 0.049 mmol) and isopropoxyltrimethylsilane (18.8 μL, 0.106 mmol). The vial was sealed again and set to stir at 400 rpm for 6 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR

spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in H_2O/ACN (23 cm packed height), and the crude product mixture containing **3h** was loaded onto the column with H_2O/ACN. 15 1-2 mL fractions were collected, dried *via* lyophilization, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* lyophilization to obtain an isolated yield of 5.3 mg (29 %). ^{1}H NMR (400 MHz, D_2O/CD_3CN): δ 7.44 (br m, 24H, OCH_2-Ar), 7.09 – 7.08 (br m, 24H, OCH_2-Ar), 5.50 (br s, 24H, O-CH_2), 3.77 – 3.68 (br m, 24H, (CONH)CH_2($CONH_2$)), 3.48 – 3.45 (br t, 12H, SCH_2CH), 3.15 – 3.10 (br m, 24H, SCH_2), 1.26 – 1.24 (d, 36H, CCH_3). ^{11}B NMR (128 MHz, D_2O/CD_3CN): δ -15.8. ^{19}F NMR (376 MHz, D_2O/CD_3CN): δ -135.4 – -135.5 (m, 24F, *-meta*), -144.7 – -144.8 (m, 24F, *-ortho*). MS (LCT Premier): *m/z* calculated for $C_{252}H_{252}B_{12}F_{48}N_{48}O_{48}S_{12}$ (M^{2-}), 3072.79 Da; found, 3072.60 Da.

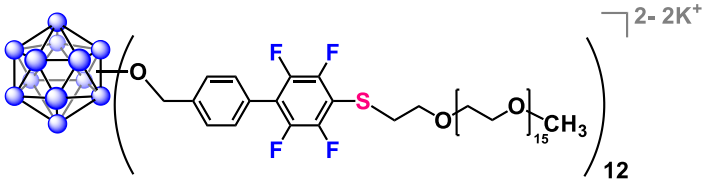
Synthesis of 3i



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (8.5 mg, 0.040 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by $mPEGthiol_{356}$ (12.27 μL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 5 hours. The vial was transferred out of the glovebox, and its contents were transferred

into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing **3i** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 17.1 mg (78 %). ^{1}H NMR (400 MHz, CD_3OD): δ 7.64 – 7.46 (br m, 24H, OCH_2-Ar), 7.26 – 7.18 (br m, 24H, OCH_2-Ar), 5.65 – 5.61 (br m, 24H, OCH_2), 3.70 (t, 24H, SCH_2CH_2), 3.62 – 3.44 (m, 288H, $SCH_2CH_2O(CH_2CH_2O)_6$), 3.30 – 3.28 (m, 36H, $(CH_2CH_2O)_6CH_3$), 3.14 (t, 24H, SCH_2). ^{11}B NMR (128 MHz, CD_3OD): δ -15.3. ^{19}F NMR (376 MHz, CD_3OD): δ -136.4 – -136.5 (m, 24F, -*meta*), -145.3 (m, 24F, -*ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{336}H_{444}B_{12}F_{48}O_{96}S_{12}$ (M^{2-}), 3721.3430 Da; found, 3721.3395 Da.

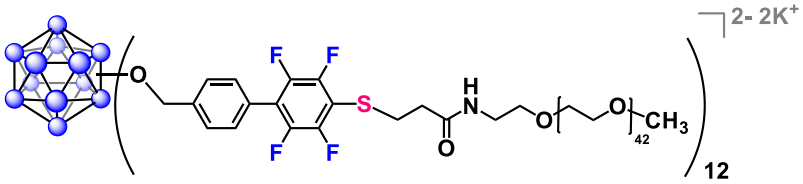
Synthesis of 3j



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (32.0 mg, 0.151 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by $mPEGthiol_{766}$ (44.1 μL, 0.063 mmol). The vial was sealed again and set to stir at 400

rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing **3j** was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried *via* rotary evaporation, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* rotary evaporation to obtain an isolated yield of 7.7 mg (21 %). ^{1}H NMR (400 MHz, CD_3OD): δ 7.57 – 7.55 (br m, 24H, OCH_2-Ar), 7.18 – 7.16 (br m, 24H, OCH_2-Ar), 5.67 – 5.62 (br m, 24H, OCH_2), 3.72 (t, 24H, SCH_2CH_2), 3.64 – 3.51 (m, 744H, $SCH_2CH_2O(CH_2CH_2O)_{15}$), 3.33 (m, 36H, $(CH_2CH_2O)_{15}CH_3$), 3.19 – 3.16 (t, 24H, SCH_2). ^{11}B NMR (128 MHz, CD_3OD): δ -15.3. ^{19}F NMR (376 MHz, CD_3OD): δ -136.1 – -136.4 (m, 24F, -*meta*), -145.1 (m, 24F, -*ortho*).

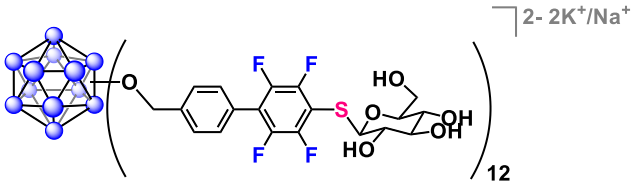
Synthesis of 3k



3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (27.0 mg, 0.127 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by $mPEGthiol_{2000}$ (85.0 mg, 0.043 mmol). The vial was sealed again and set to stir at 400 rpm for 20 hours. The vial was transferred out of the glovebox, and its contents were transferred

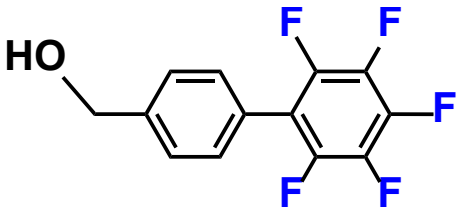
into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing **3k** was loaded onto the column with water. 15 1-2 mL fractions were collected, dried *via* lyophilization, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* lyophilization to obtain an isolated yield of 43.2 mg (54 %). ^{1}H NMR (400 MHz, CD_3OD): δ 7.64 – 7.47 (br m, 24H, OCH_2-Ar), 7.20 (br m, 24H, OCH_2-Ar), 5.66 (br m, 24H, OCH_2), 3.92 – 3.44 (m, 2100H, $SCH_2CH_2(CONH)CH_2CH_2O(CH_2CH_2O)_{42}$), 3.35 (s, 36H, $(CH_2CH_2O)_{42}CH_3$), 3.19 (t, 24H, SCH_2-CH_2). ^{11}B NMR (128 MHz, CD_3OD): δ -15.4. ^{19}F NMR (376 MHz, CD_3OD): δ -136.2 – -137.3 (m, 24F, -*meta*), -145.0 – -145.5 (m, 24F, -*ortho*). GPC trace of **3k** measured in water with 0.02% NaN_3 at 12 °C gives a Đ (polydispersity index) of 1.081 (see Fig. 3c in main text).

Synthesis of 3l

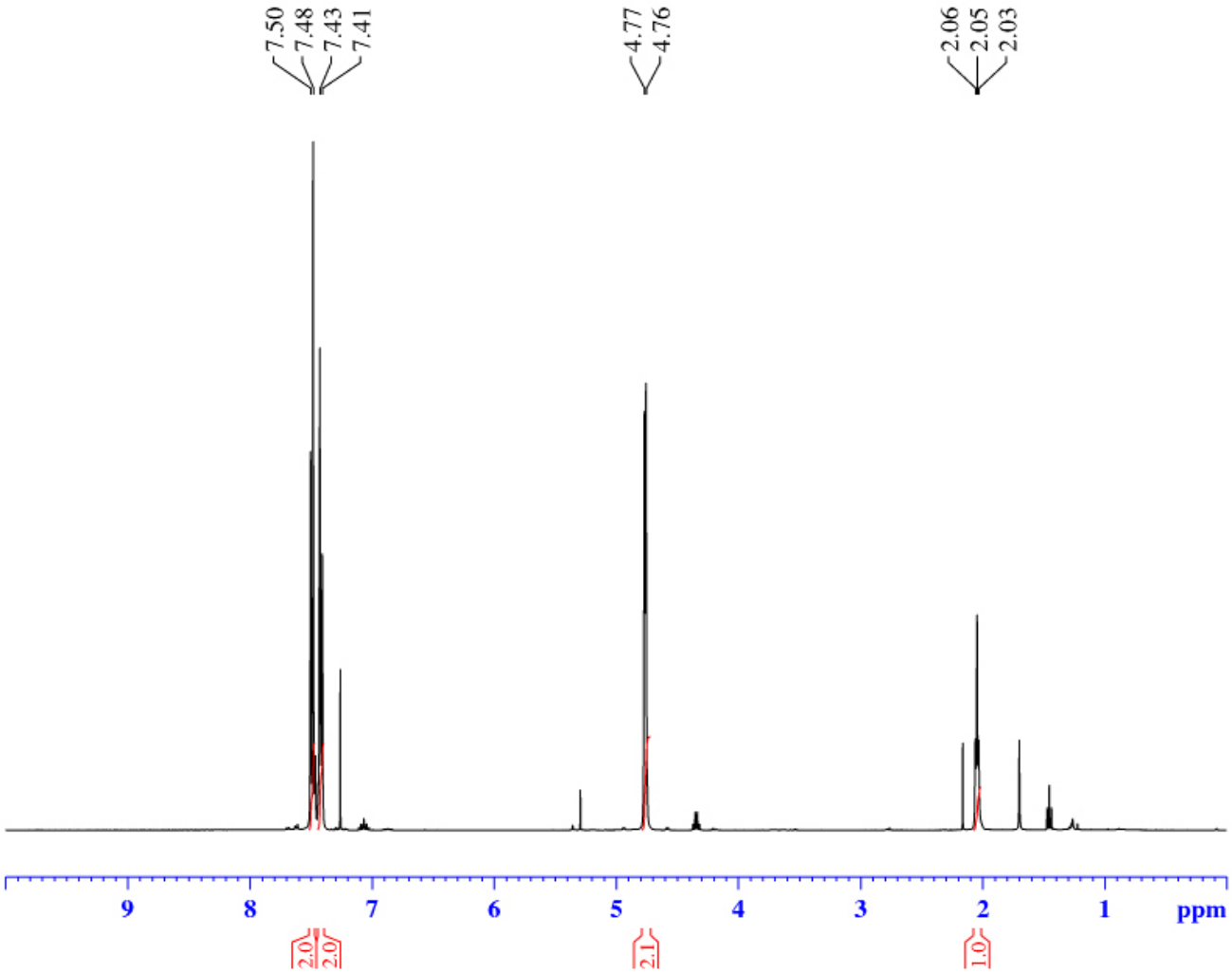


3 (10.0 mg, 0.0029 mmol) and K_3PO_4 (18.7 mg, 0.088 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N_2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 μL anhydrous DMF was added, followed by 1-thio-β-D-glucose tetraacetate (16.4 mg, 0.045 mmol). The vial was sealed again and

set to stir at 400 rpm for 5 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* ^{19}F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* ^{11}B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. The resulting residue was treated with NaOMe (3.8 mg, 0.07 mmol) in 1 mL MeOH for 2 hours. The volatiles were removed *via* rotary evaporation. The crude product mixture containing **3l** was dissolved in water and adjusted to pH 7.3 using 3M HCl. This mixture was then centrifuged 5 times – after each of the first 4 centrifugation periods, the supernatant was removed by pipet and more water was added, after the 5th centrifugation period, the supernatant was removed and the precipitate was dried *via* lyophilization, and subjected to characterization *via* ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy. This pure product as indicated by NMR spectroscopy was dried *via* lyophilization to obtain an isolated yield of 5.3 mg (32 %). ^{1}H NMR (400 MHz, CD_3OD): δ 7.62 – 7.46 (br m, 24H, OCH_2-Ar), 7.27 – 7.17 (br m, 24H, OCH_2-Ar), 5.65 – 5.56 (br m, 24H, OCH_2), 3.77 – 3.33, 3.28 (m, 84H, $SCHCH_2OH(CHOH)_3CHO$). ^{11}B NMR (128 MHz, CD_3OD): δ -15.4. ^{19}F NMR (376 MHz, CD_3OD): δ -135.4 – -135.5 (m, 24F, *-meta*), -145.5 – -145.6 (m, 24F, *-ortho*). HRMS (Q-Exactive Plus): *m/z* calculated for $C_{228}H_{204}B_{12}F_{48}O_{72}S_{12}$ (M^{3-}), 1840.3100 Da; found, 1840.3178 Da.



^{1}H NMR

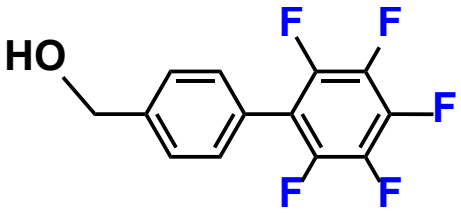


Current Data Parameters
NAME G2-OH
EXPNO 80
PROCNO 1

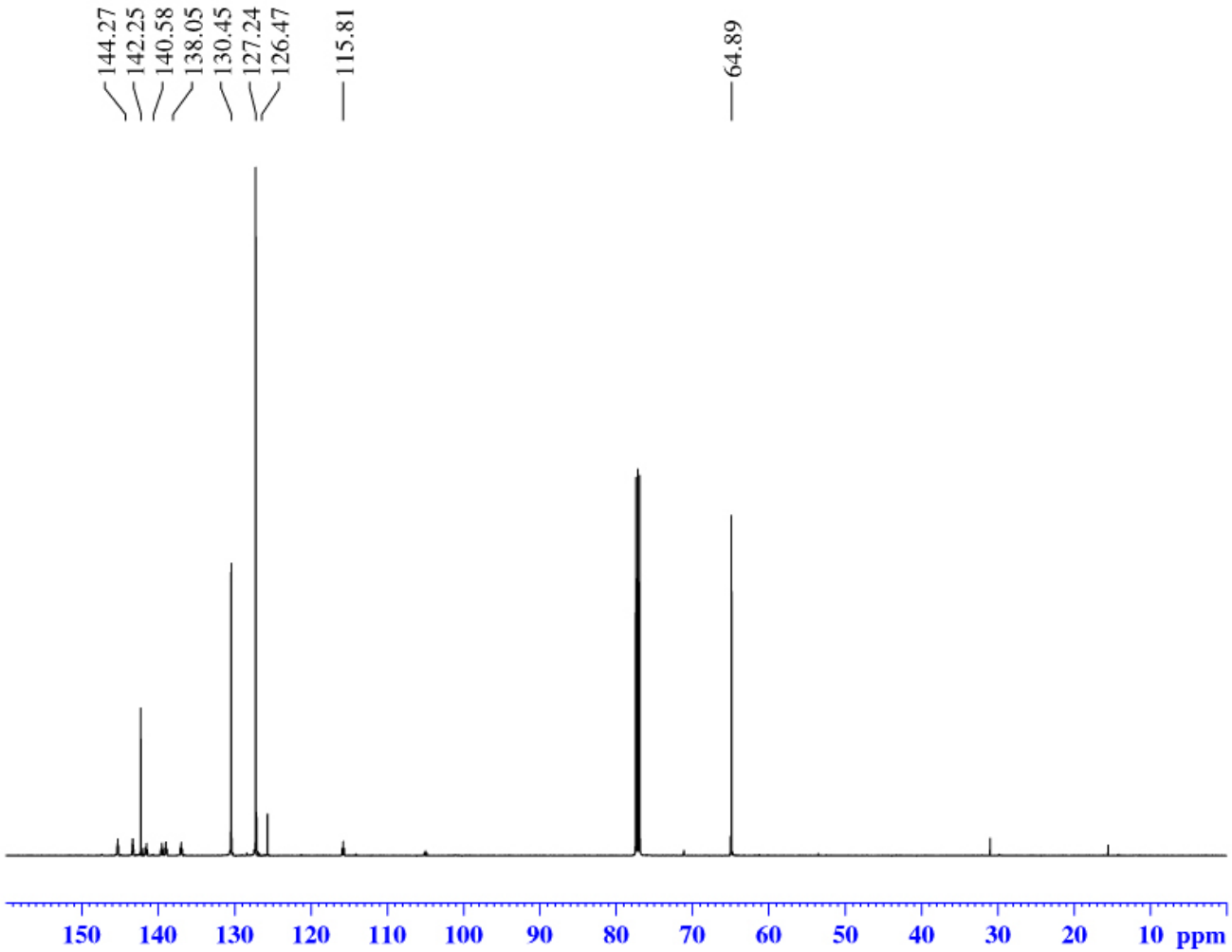
F2 - Acquisition Parameters
Date_ 20160805
Time 2.22
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 80
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



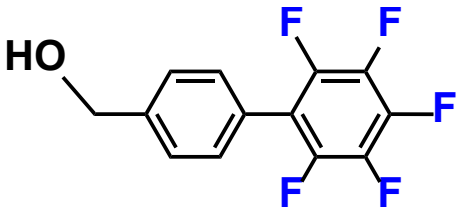
$^{13}C\{^{1}H\}$ NMR



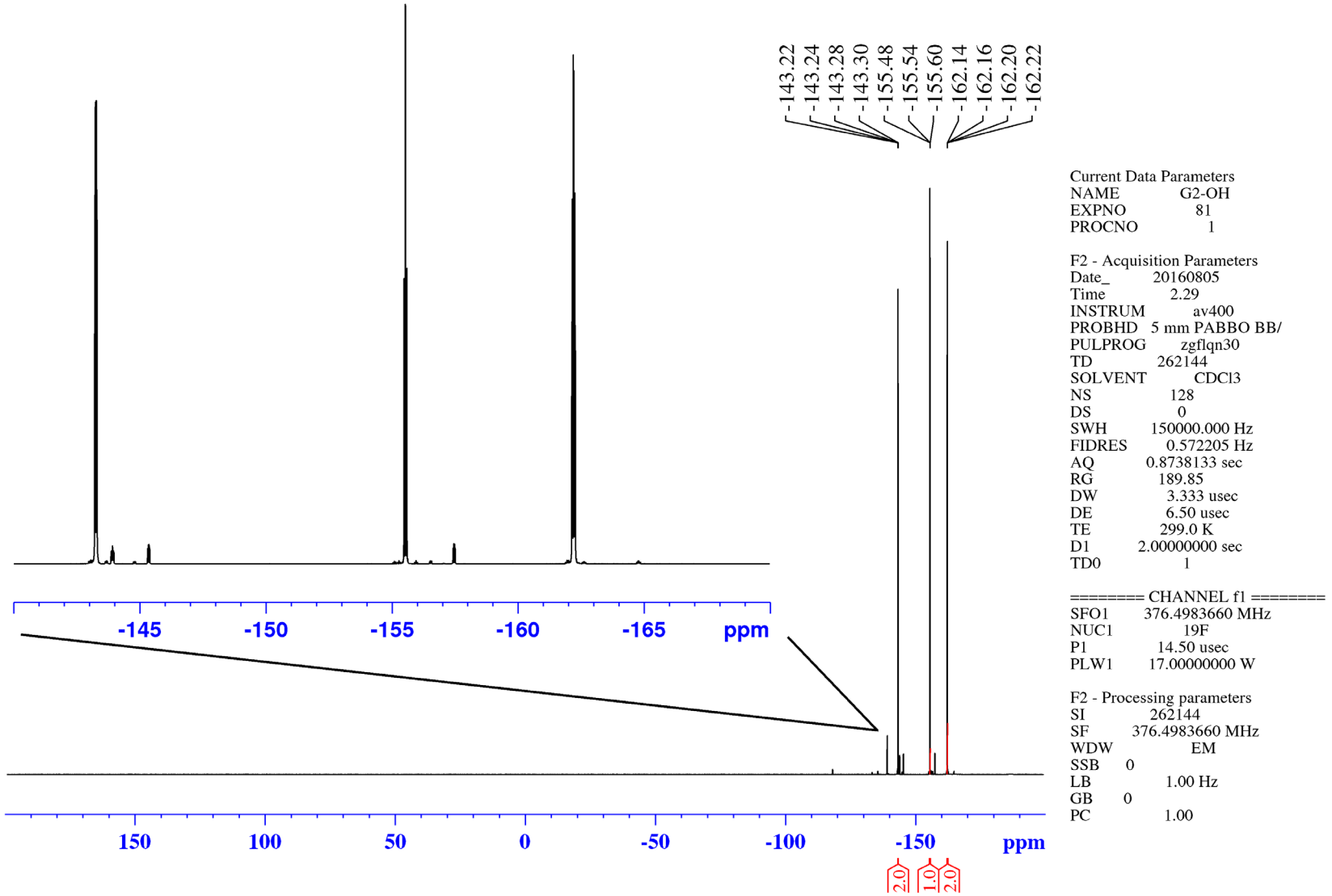
Current Data Parameters
NAME G2-OH
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160805
Time 14.25 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 475
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577740 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



^{19}F NMR

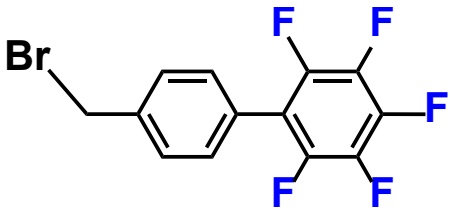


Current Data Parameters
NAME G2-OH
EXPNO 81
PROCNO 1

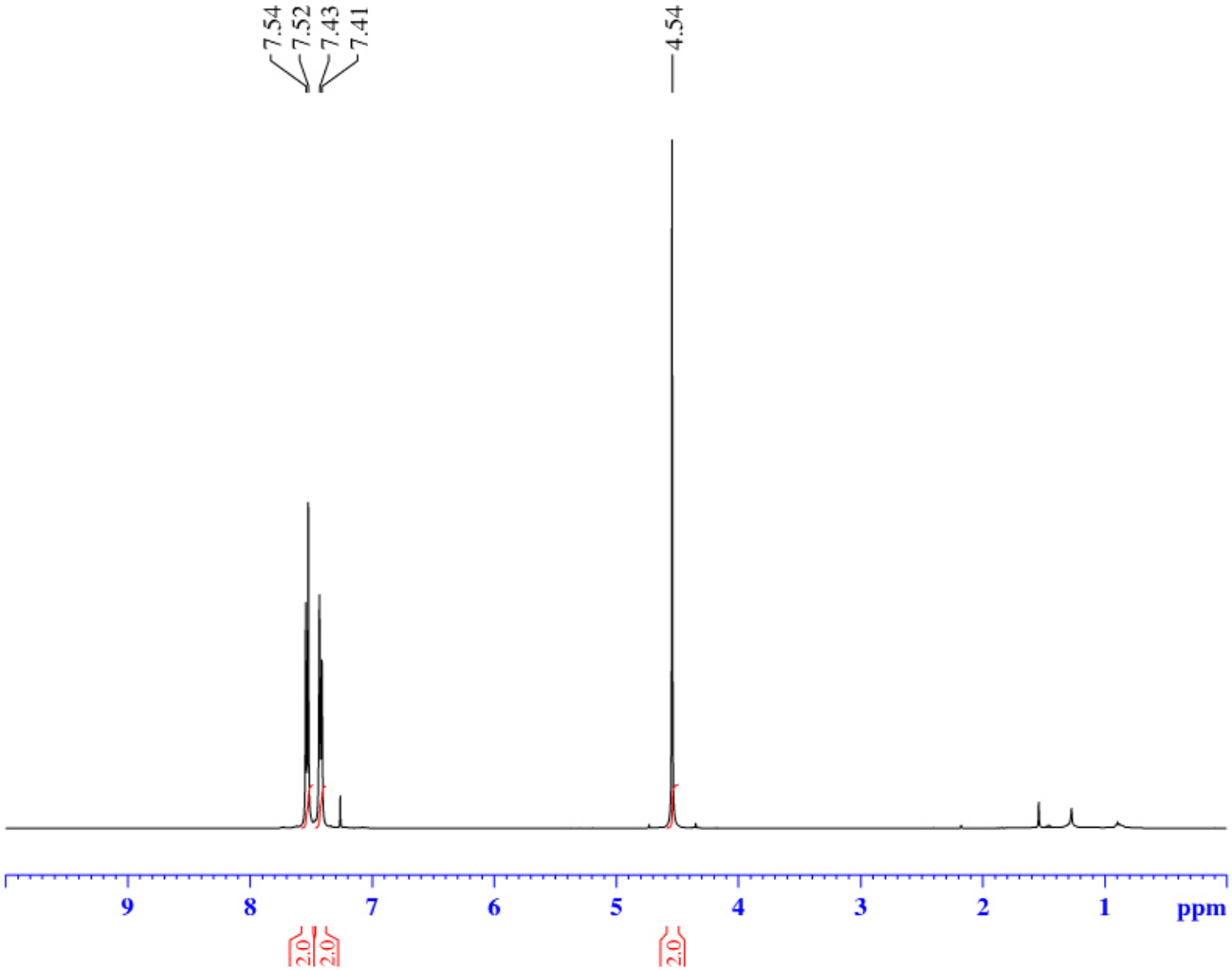
F2 - Acquisition Parameters
Date_ 20160805
Time 2.29
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CDCl3
NS 128
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

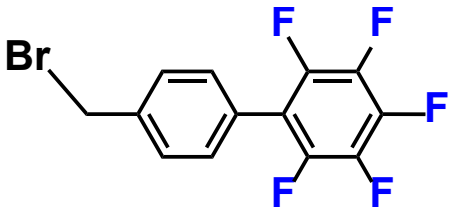


Current Data Parameters
NAME G2-Br
EXPNO 30
PROCNO 1

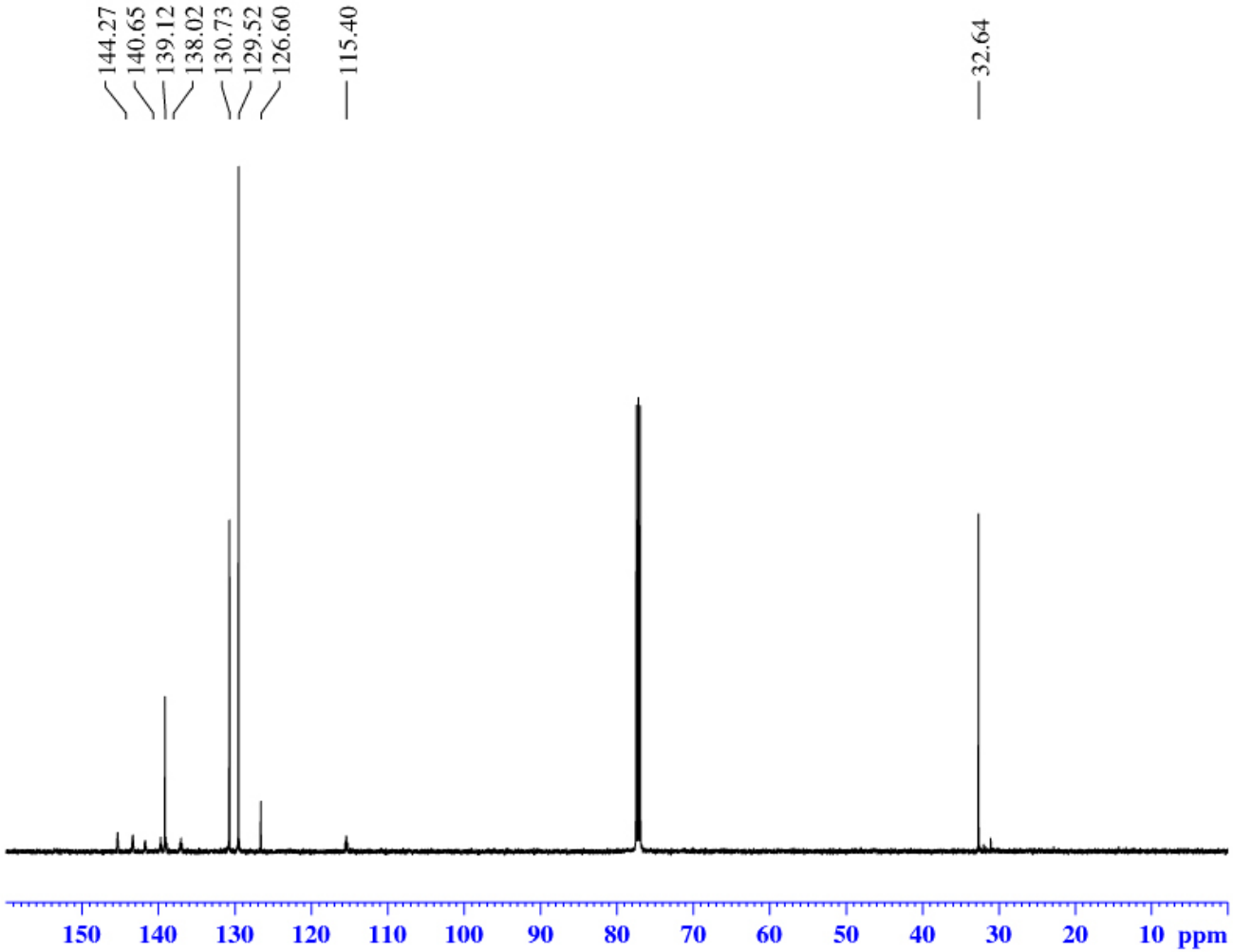
F2 - Acquisition Parameters
Date_ 20160523
Time 11.42
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 48
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 73.86
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



$^{13}C\{^{1}H\}$ NMR



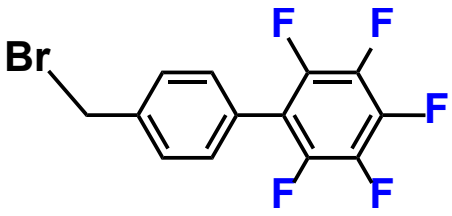
Current Data Parameters
NAME Saebi_G2-Br
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160806
Time 13.30
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1186
DS 0
SWH 32679.738 Hz
FIDRES 0.498653 Hz
AQ 1.0027008 sec
RG 14596.5
DW 15.300 usec
DE 6.00 usec
TE 298.1 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1

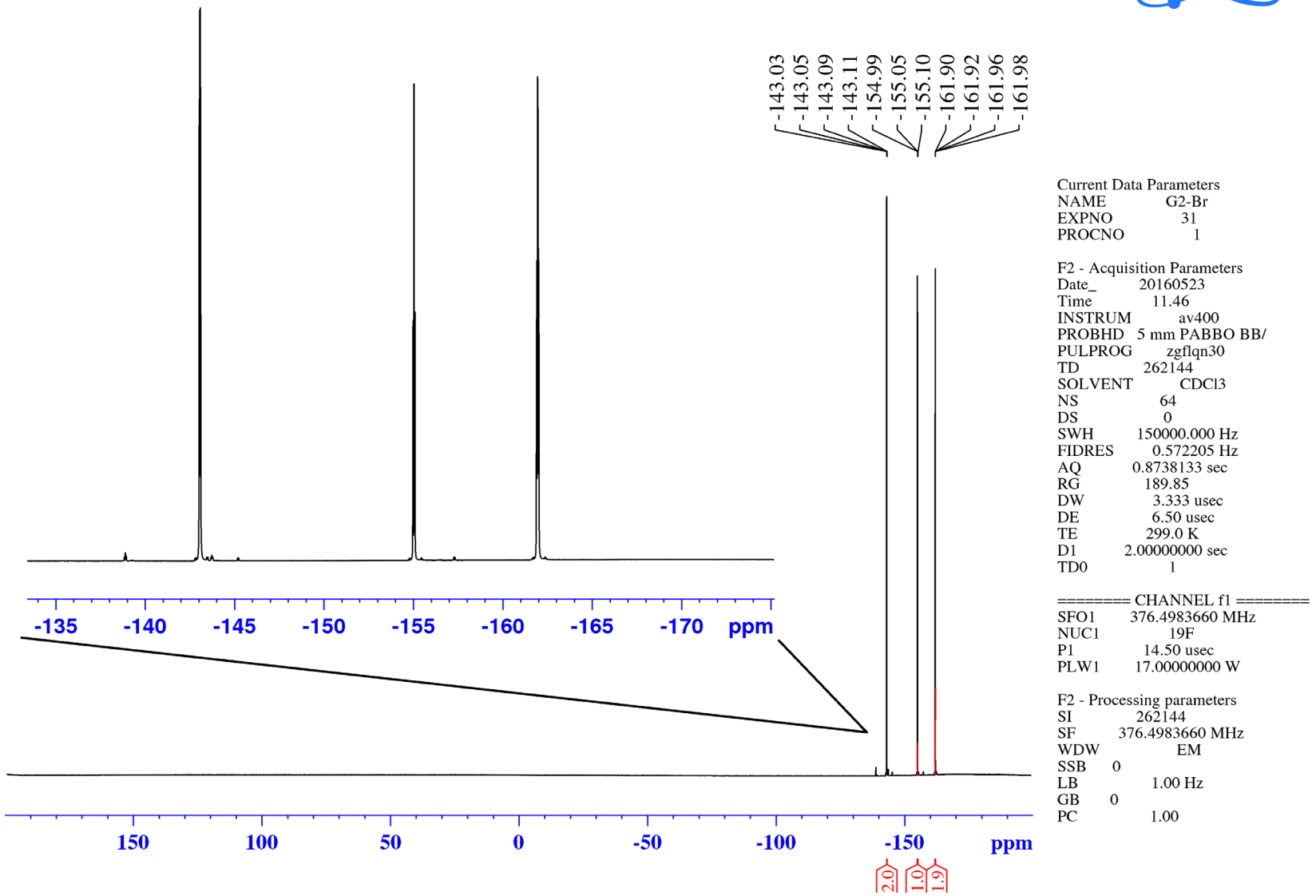
======== CHANNEL f1 ========
NUC1 13C
P1 6.50 usec
PL1 0 dB
SFO1 125.8231939 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0 dB
PL12 17.52 dB
SFO2 500.3320013 MHz

F2 - Processing parameters
SI 65536
SF 125.8080650 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



^{19}F NMR

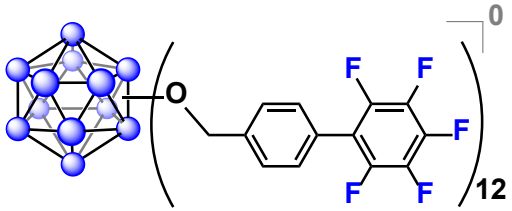


Current Data Parameters
NAME G2-Br
EXPNO 31
PROCNO 1

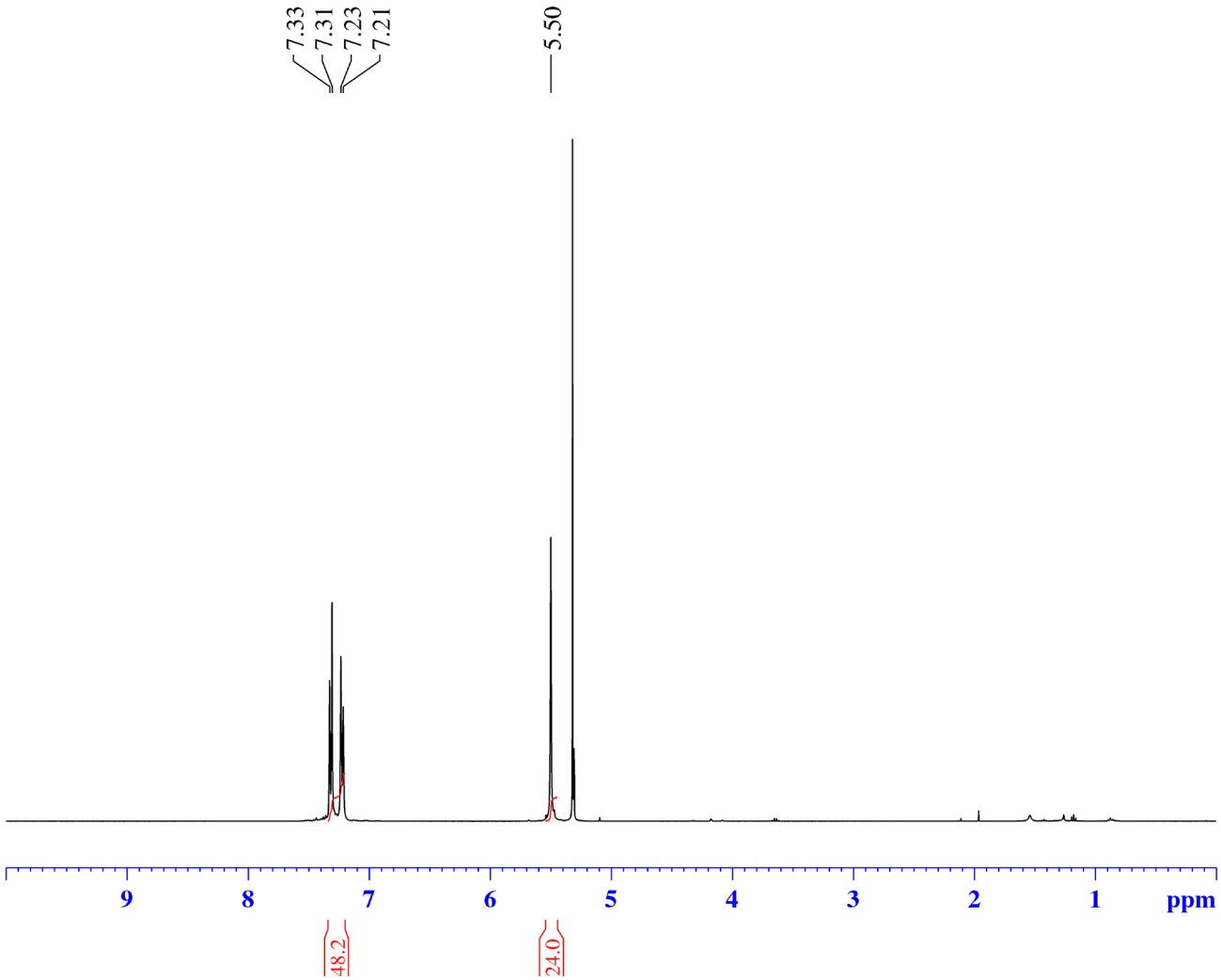
F2 - Acquisition Parameters
Date_ 20160523
Time 11.46
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CDCl3
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

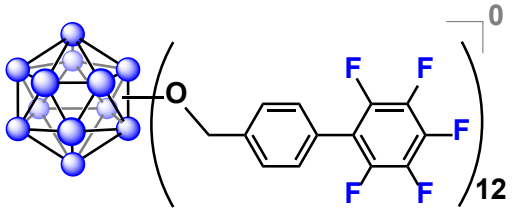


Current Data Parameters
NAME B12(O-PhPFBn)12 aka Gen2
EXPNO 91
PROCNO 1

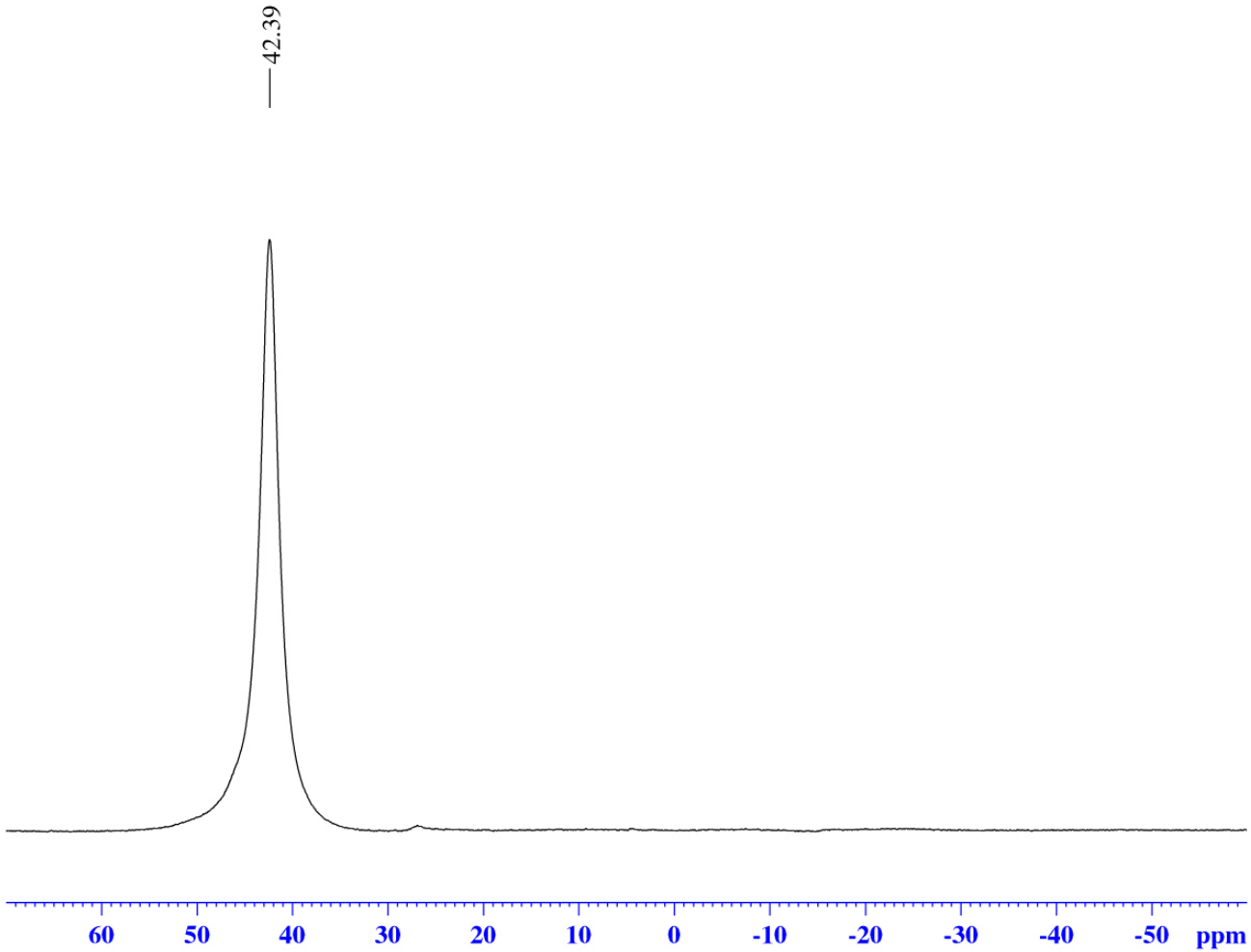
F2 - Acquisition Parameters
Date_ 20151220
Time 14.27
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CD2Cl2
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300203 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B {^{1}H} NMR



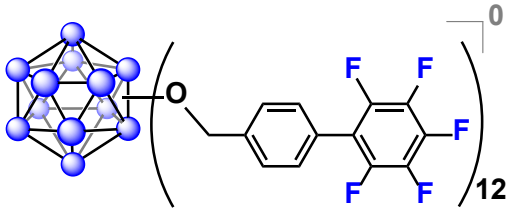
Current Data Parameters
NAME B12(O-PhPFBn)12 aka Gen2
EXPNO 90
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151220
Time 14.23
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgdc.js
TD 5096
SOLVENT CD2Cl2
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
D11 0.03000000 sec
TD0 1

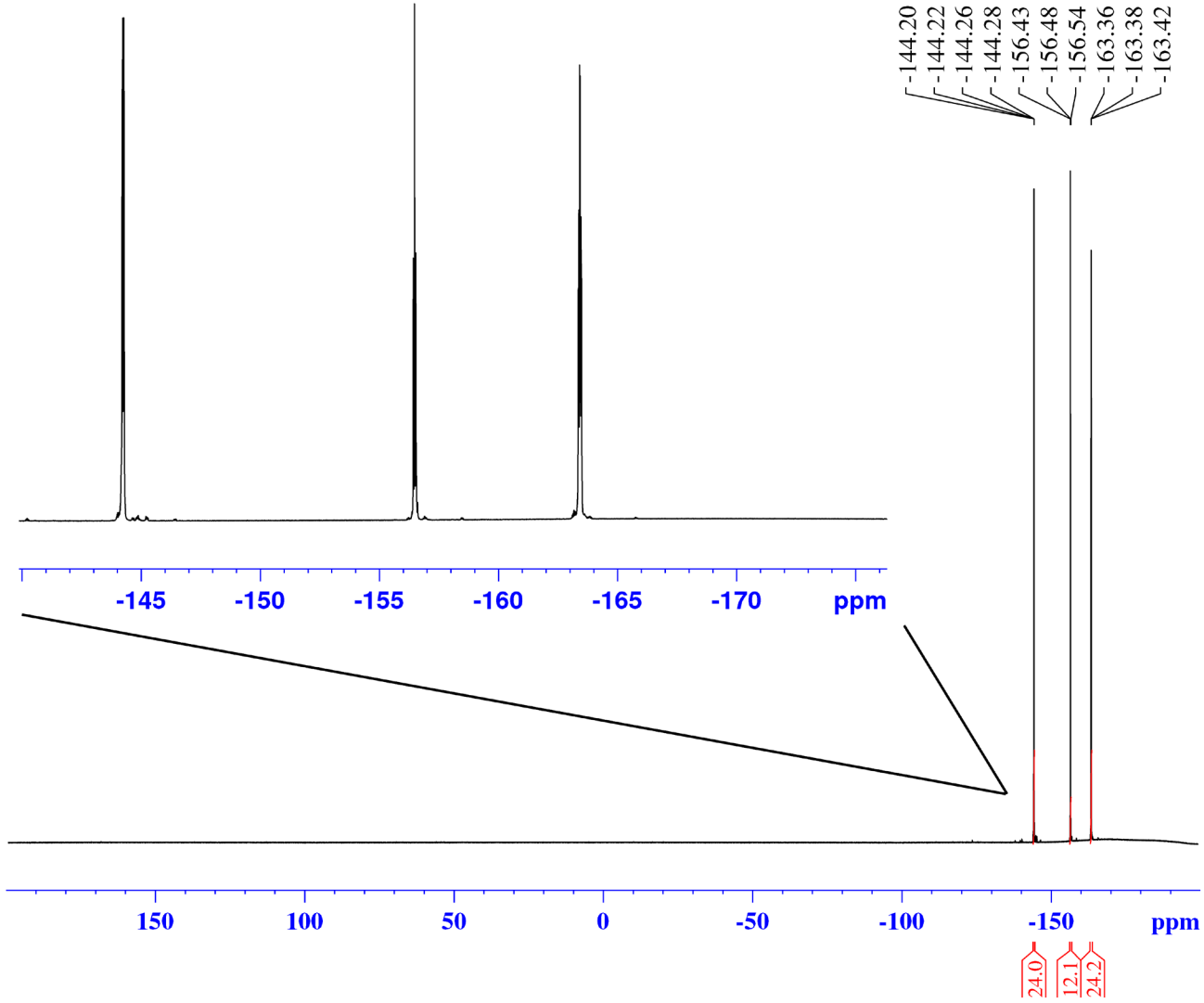
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

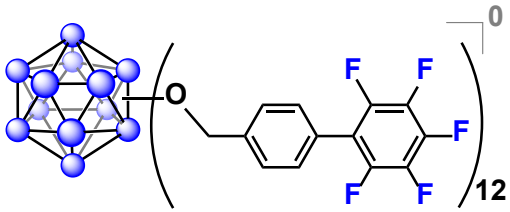


Current Data Parameters
NAME B12(O-PhPFBn)12 aka Gen2
EXPNO 92
PROCNO 1

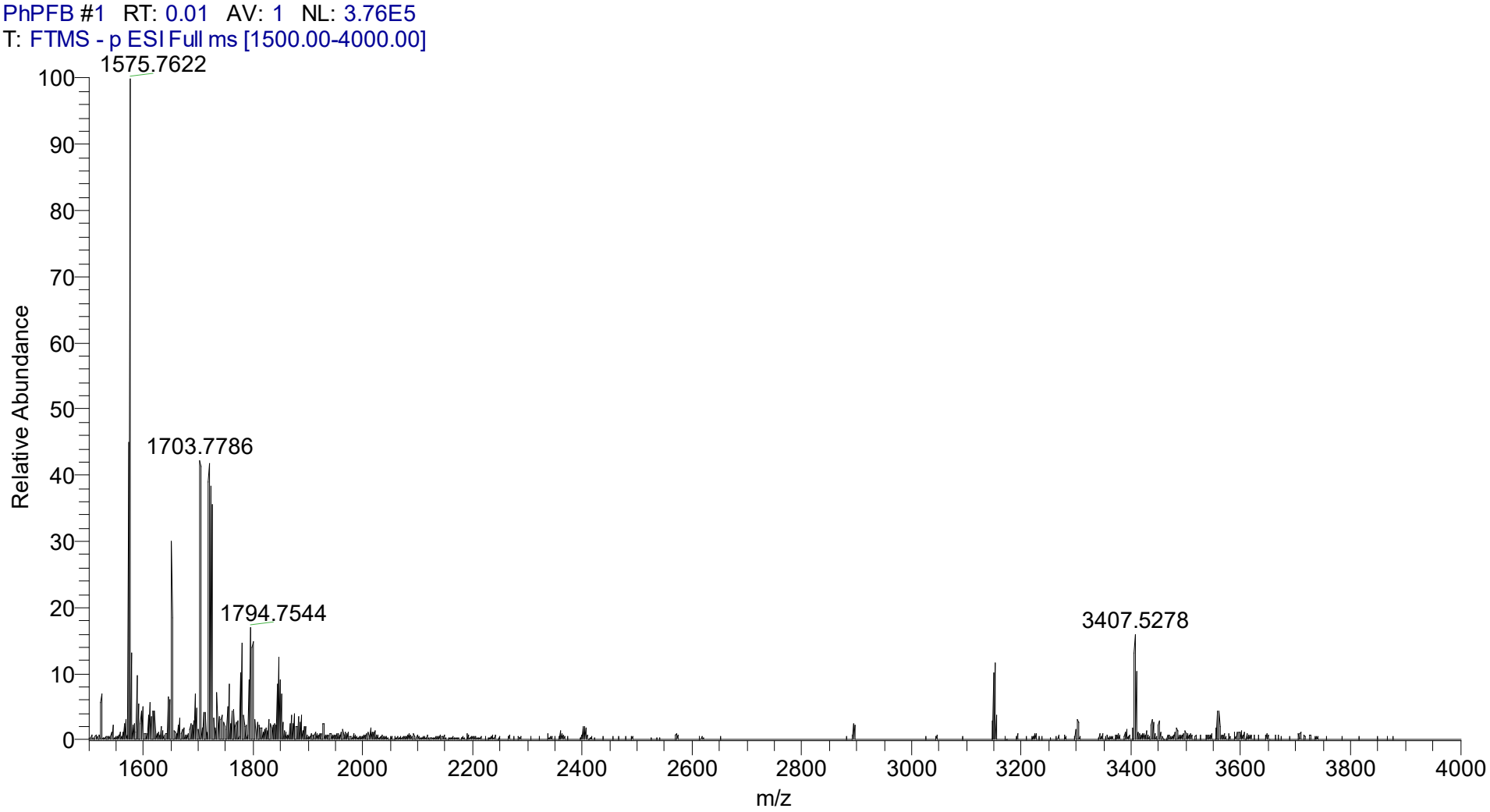
F2 - Acquisition Parameters
Date_ 20151220
Time 14.33
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD2Cl2
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

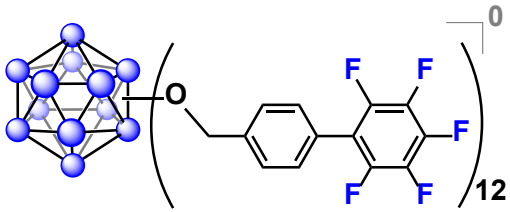
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



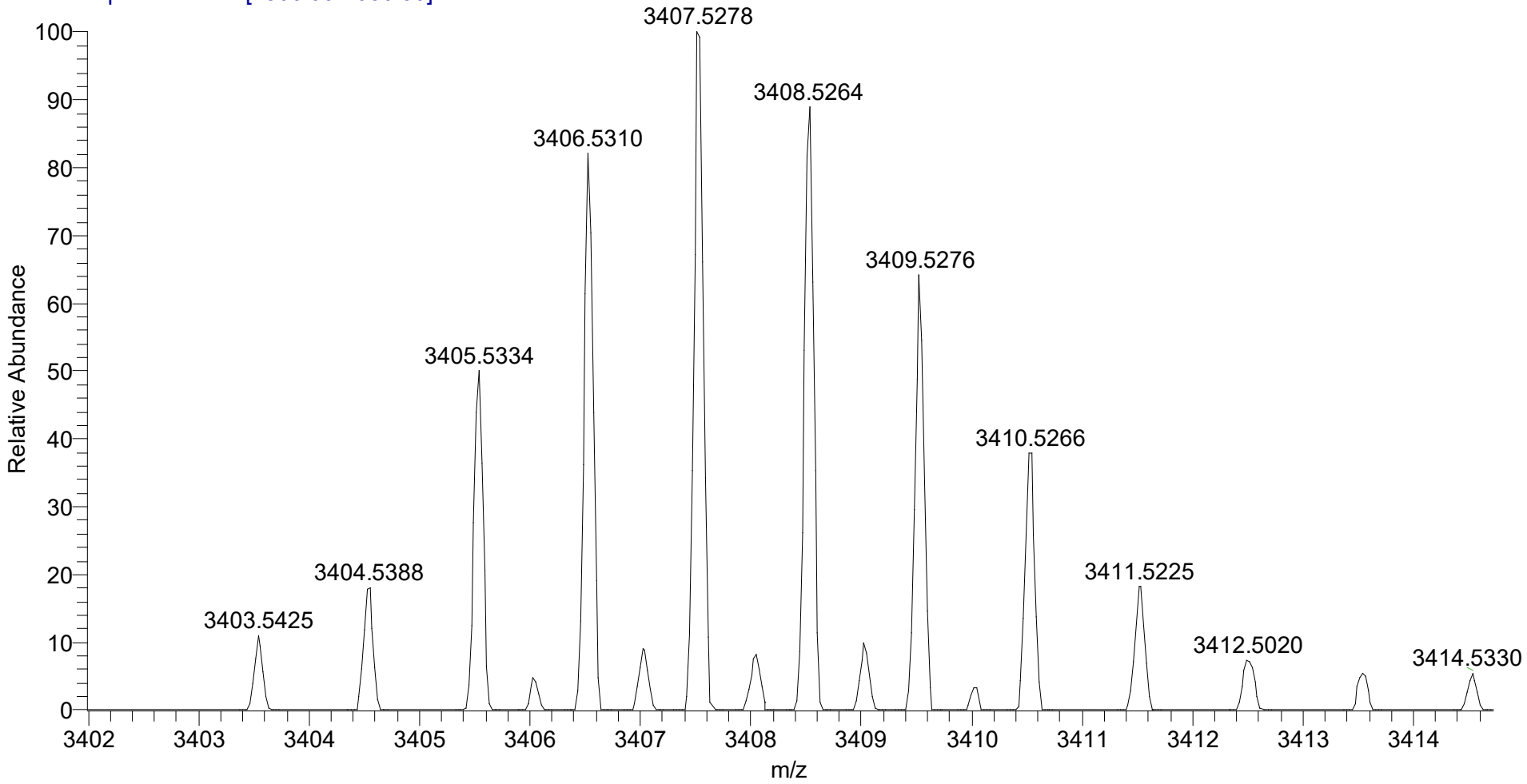
Q Exactive
High-Res Mass Spec

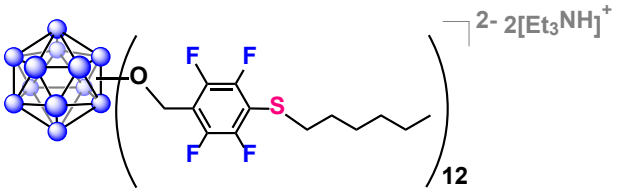




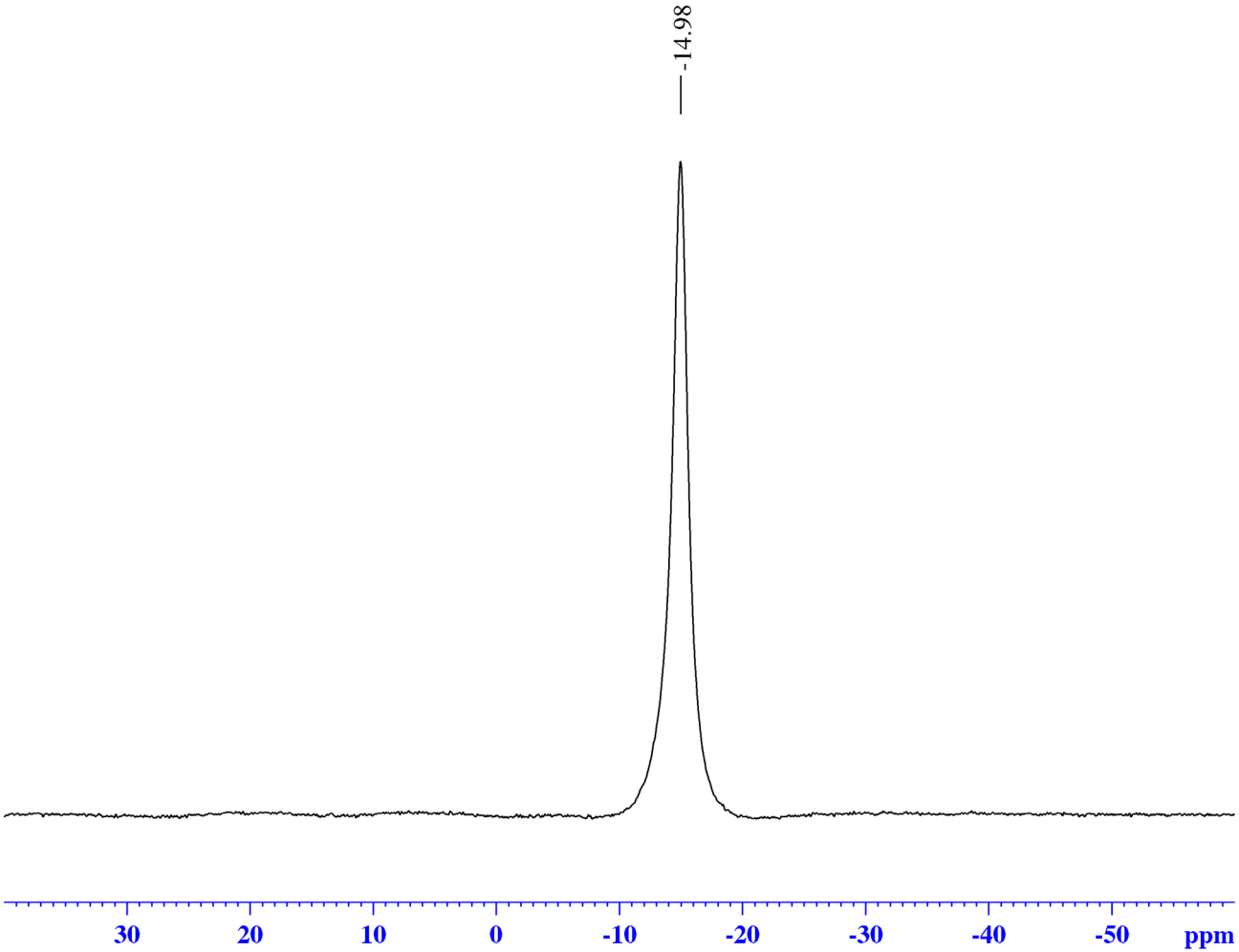
Q Exactive
High-Res Mass Spec

PhPFB #1 RT: 0.01 AV: 1 NL: 6.03E4
T: FTMS - p ESI Full ms [1500.00-4000.00]





in situ ^{11}B NMR

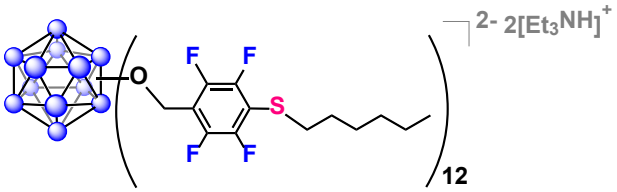


Current Data Parameters
NAME 0219
EXPNO 31
PROCNO 1

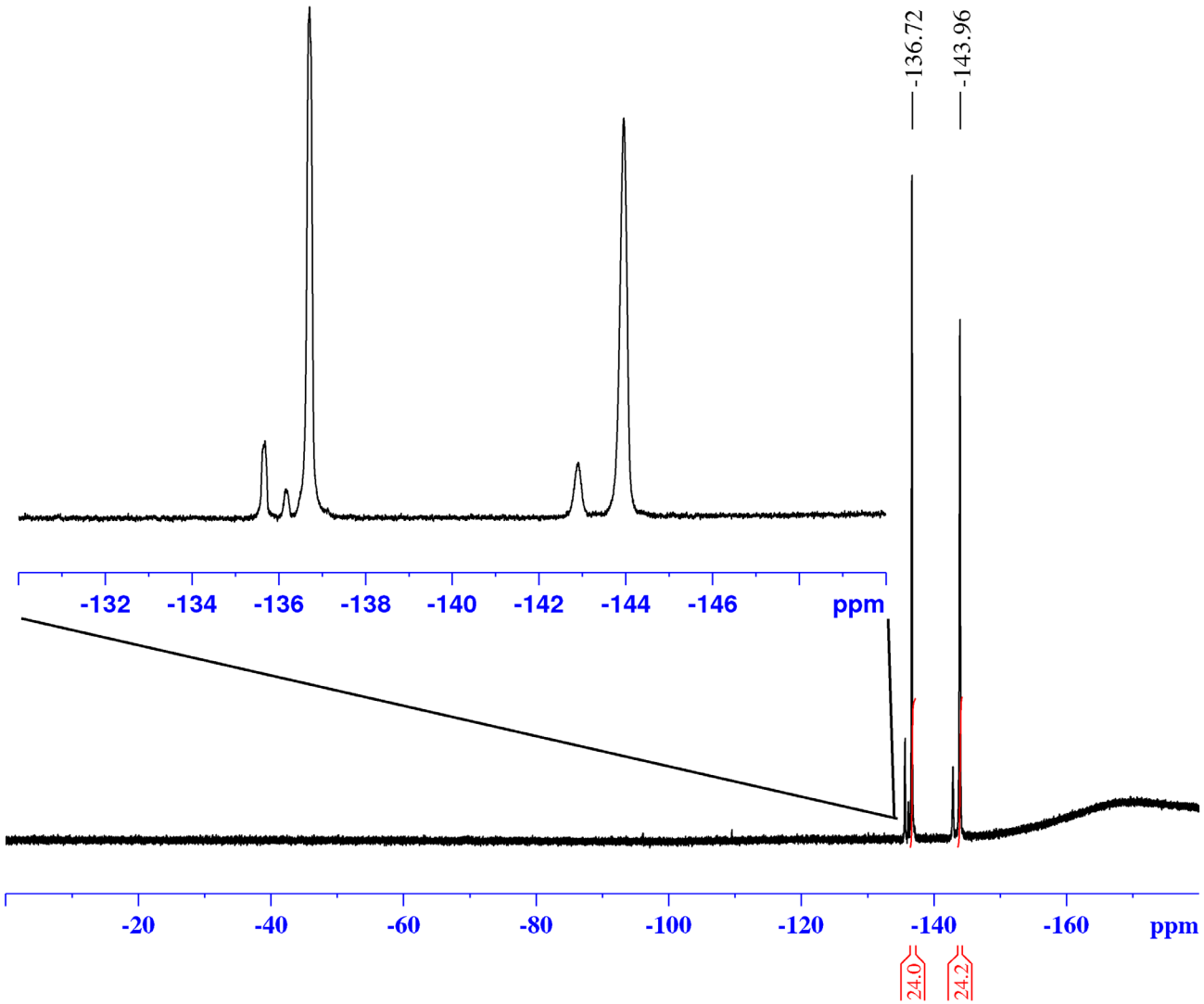
F2 - Acquisition Parameters
Date_ 20160219
Time 11.46
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR



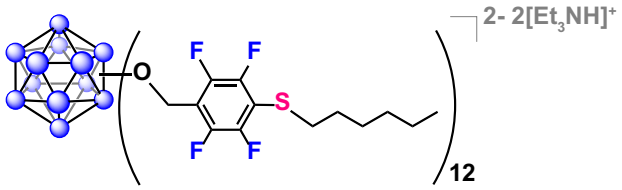
Current Data Parameters
NAME 0219
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160219
Time 11.42
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

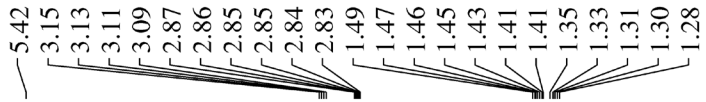
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

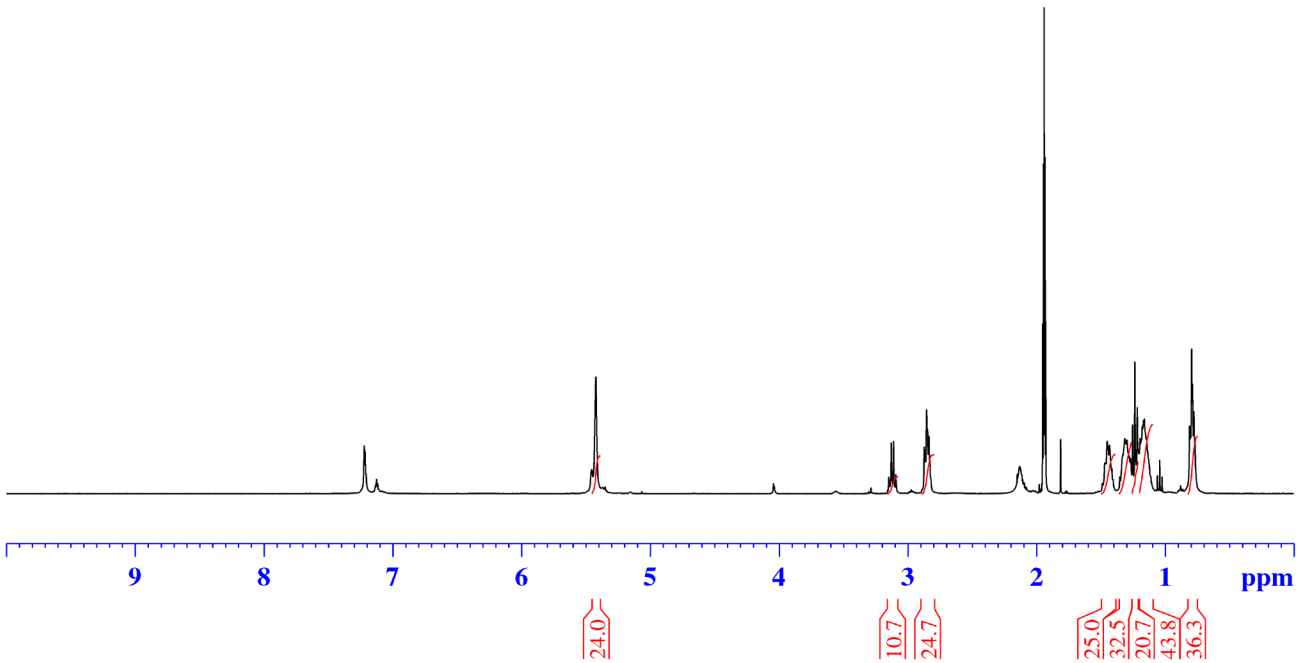
F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

Small impurities are present due to the commercial 1-hexanethiol used (95% pure).



^{1}H NMR



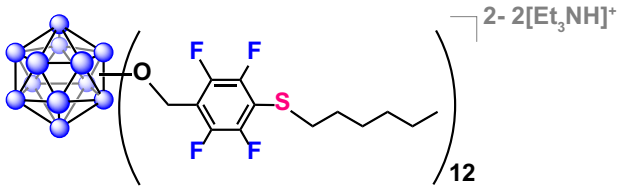


Current Data Parameters
NAME Feb23-2016
EXPNO 52
PROCNO 1

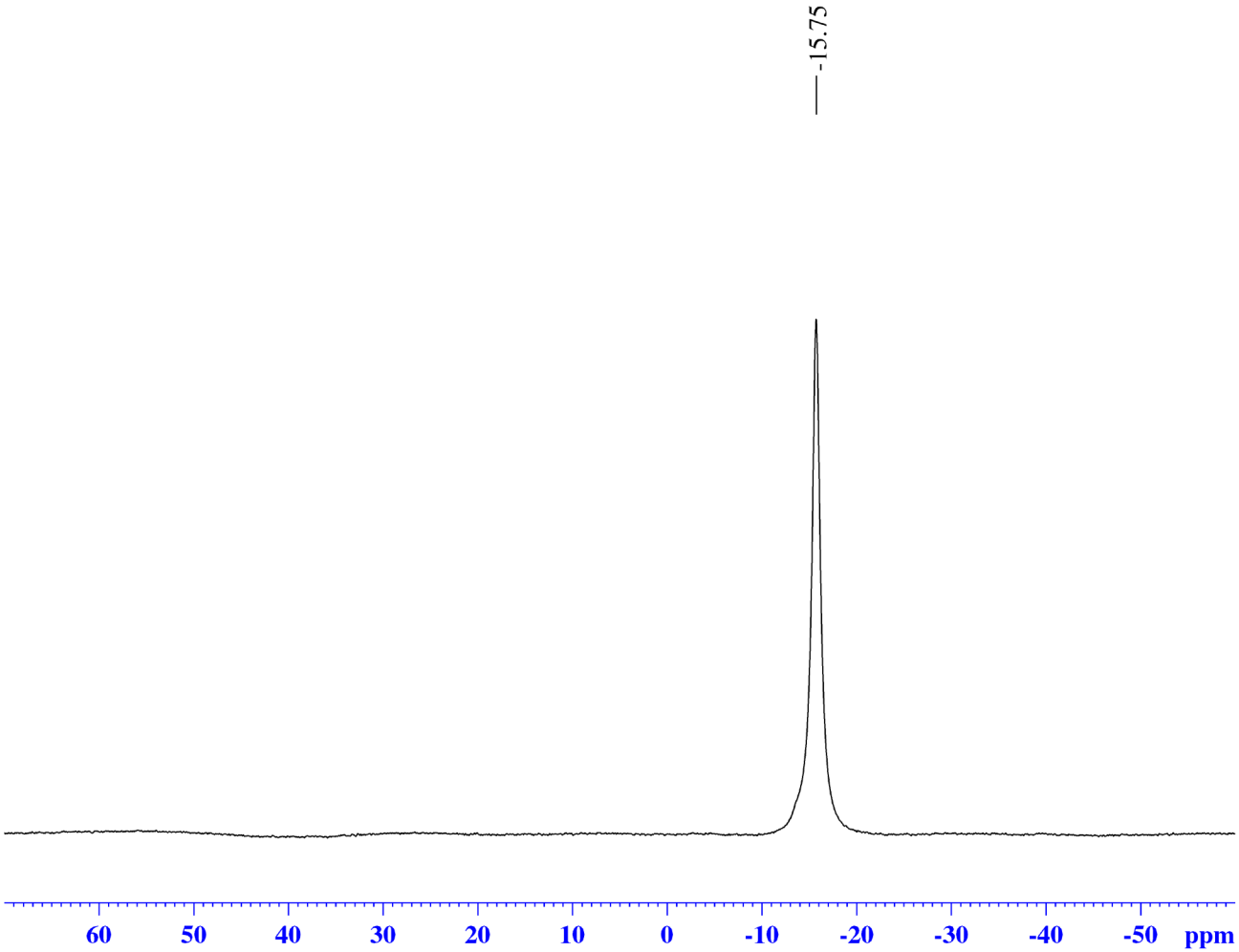
F2 - Acquisition Parameters
Date_ 20160223
Time 11.30
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 160254
SOLVENT CD3CN
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.050001 Hz
AQ 9.9998493 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300112 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B {^{1}H} NMR



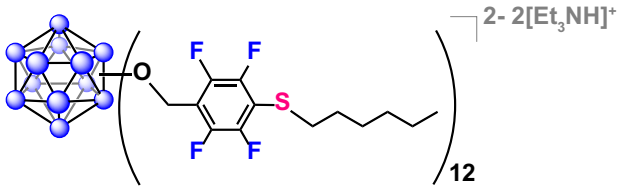
Current Data Parameters
NAME Feb23-2016
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160223
Time 11.14
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgdc.js
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.1 K
D1 0.05000000 sec
D11 0.03000000 sec
TD0 1

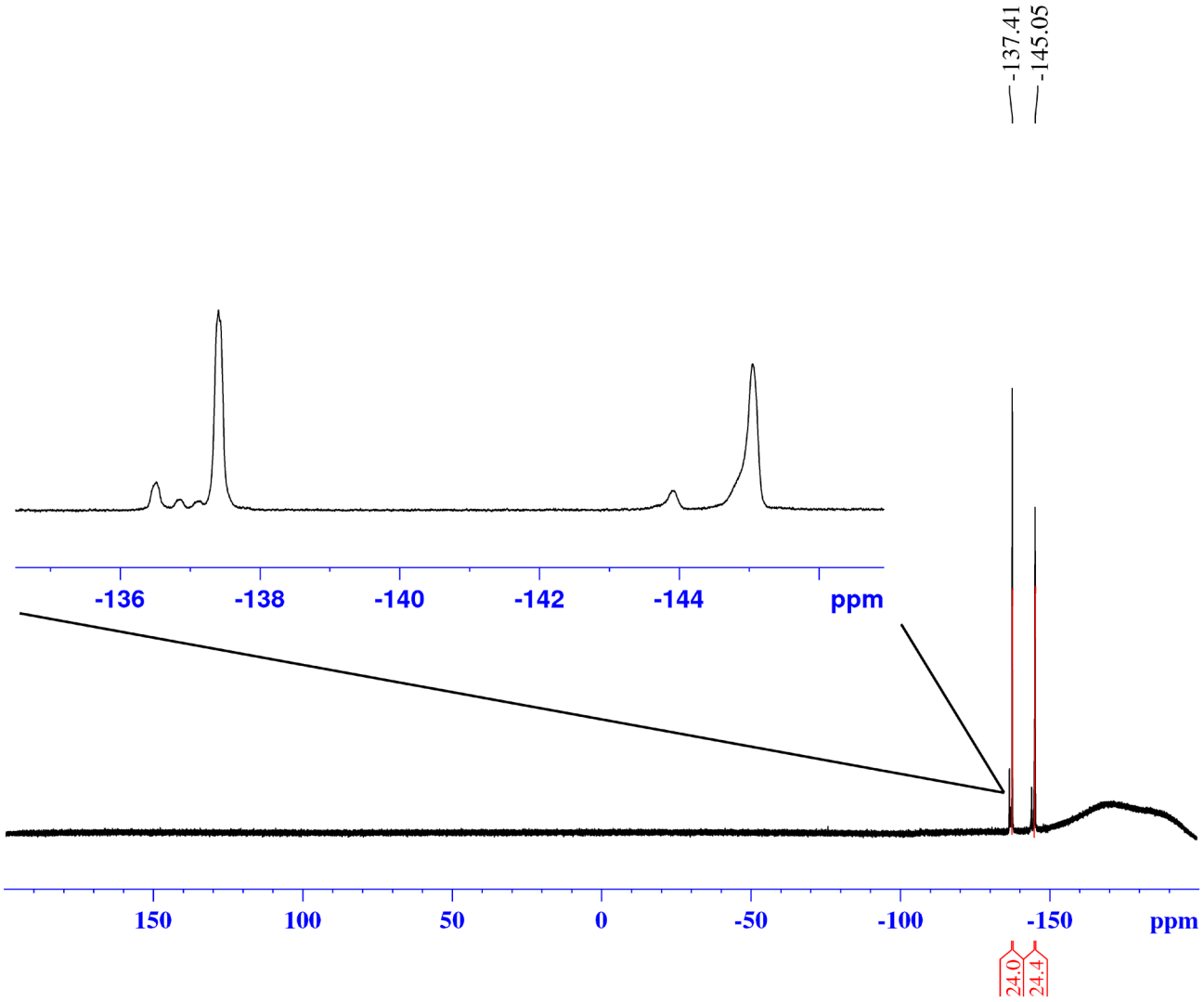
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR



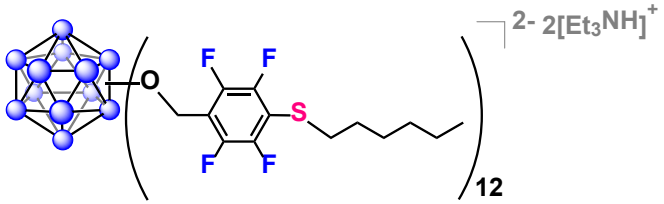
Current Data Parameters
NAME Feb23-2016
EXPNO 51
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160223
Time 11.18
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

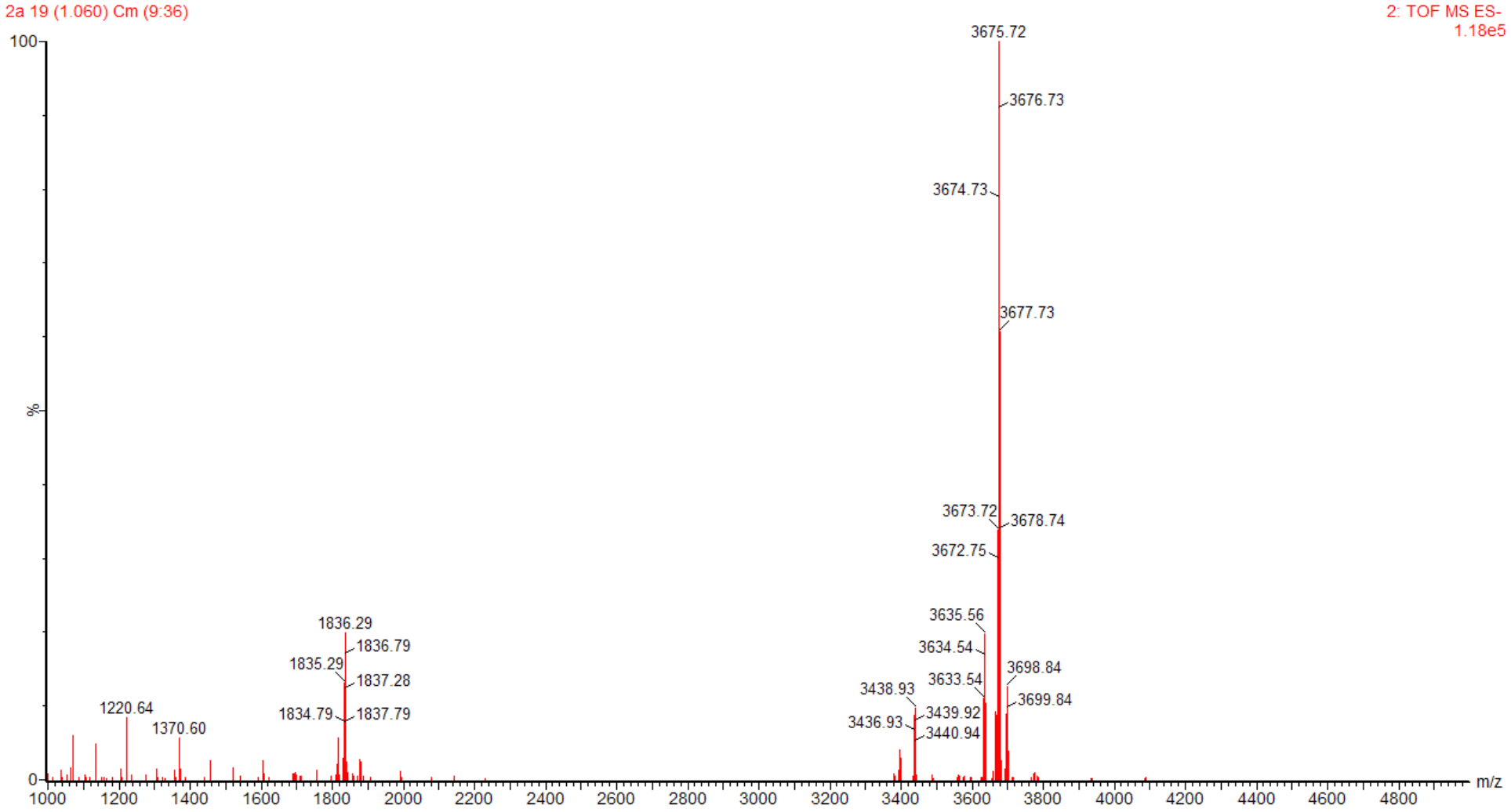
F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

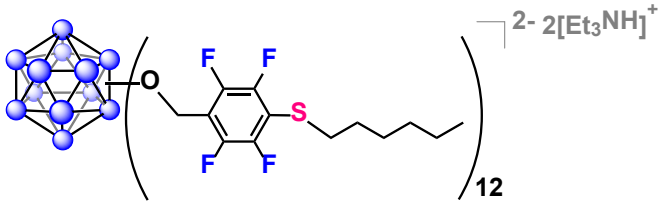
Small impurities are present due to the commercial 1-hexanethiol used (95% pure).



Waters
Mass Spec

high mz scan
2a 19 (1.060) Cm (9:36)



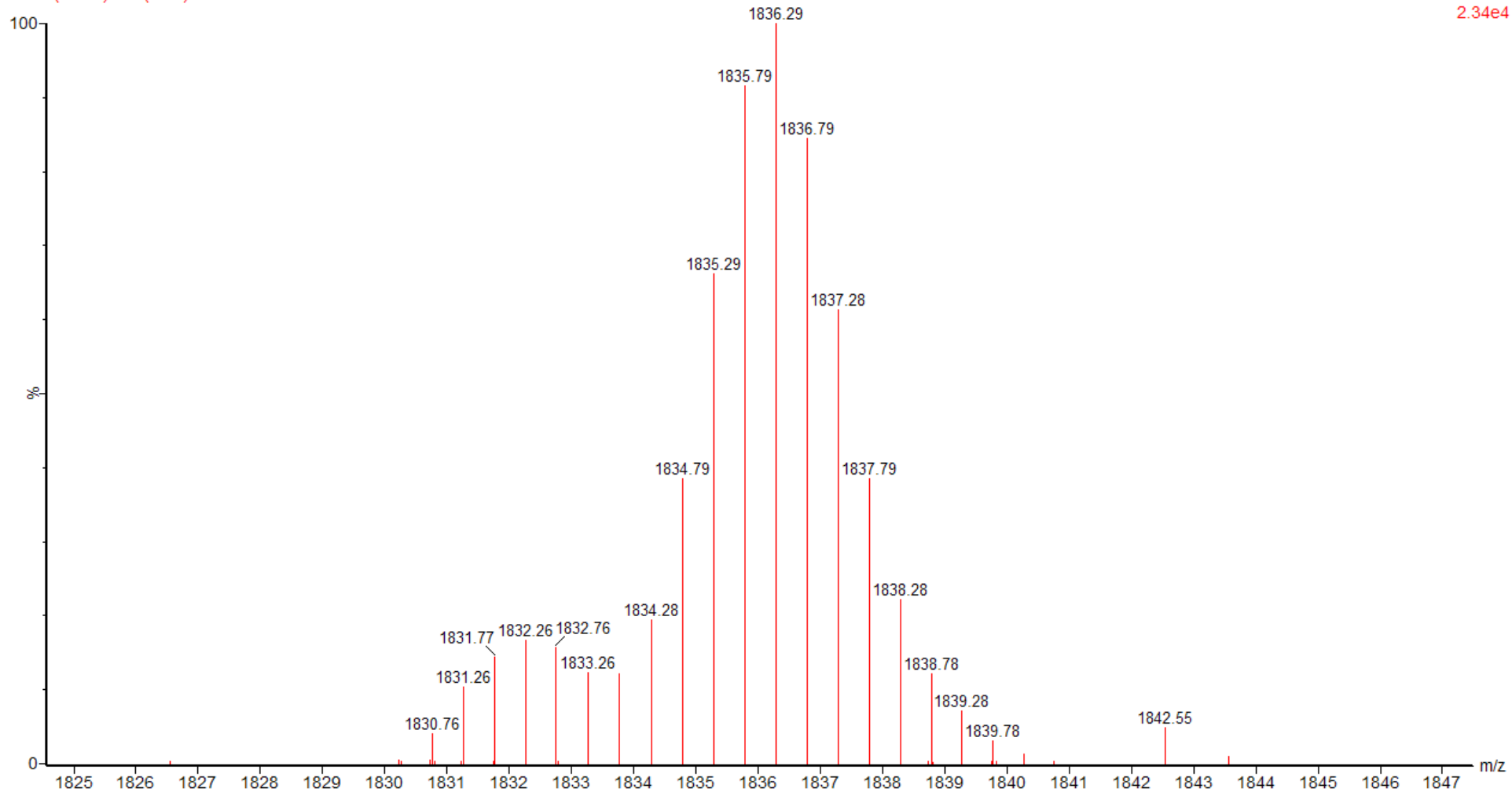


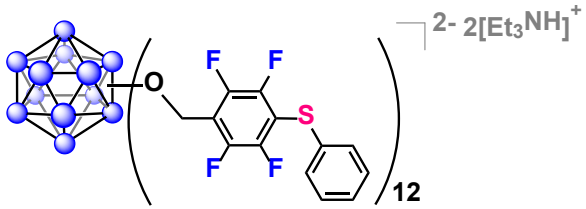
Waters Mass Spec

high mz scan

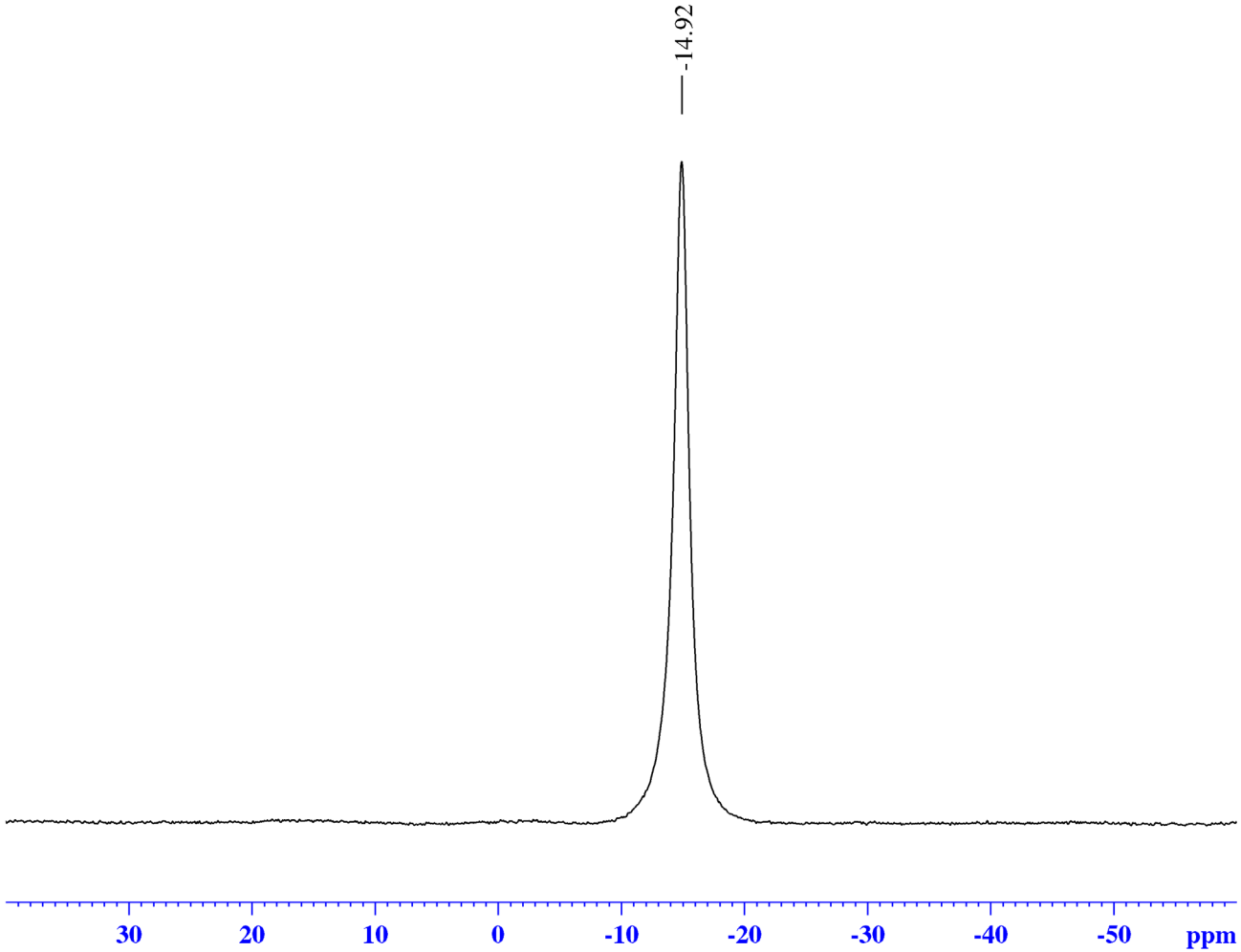
2a 19 (1.060) Cm (9:36)

2: TOF MS ES-
2.34e4





in situ ^{11}B NMR

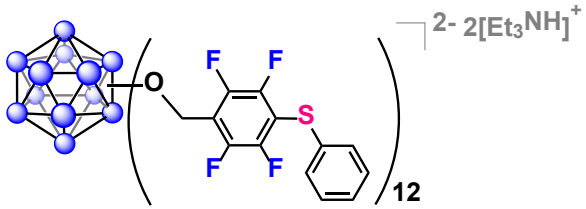


Current Data Parameters
NAME 0129
EXPNO 221
PROCNO 1

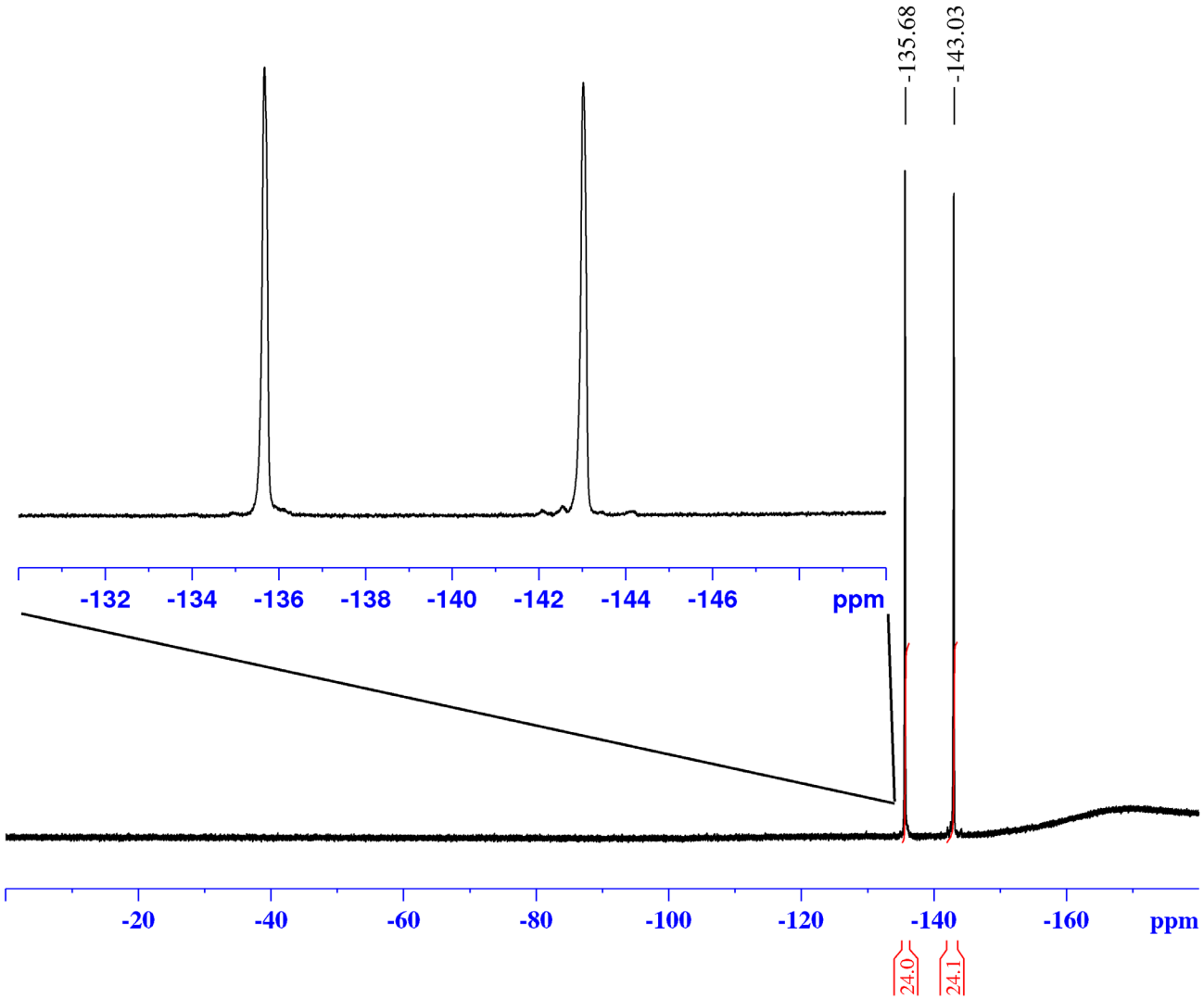
F2 - Acquisition Parameters
Date_ 20160129
Time 20.43
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

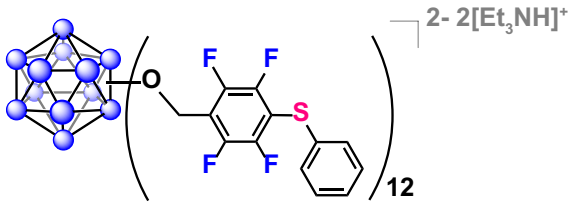


Current Data Parameters
NAME 0129
EXPNO 220
PROCNO 1

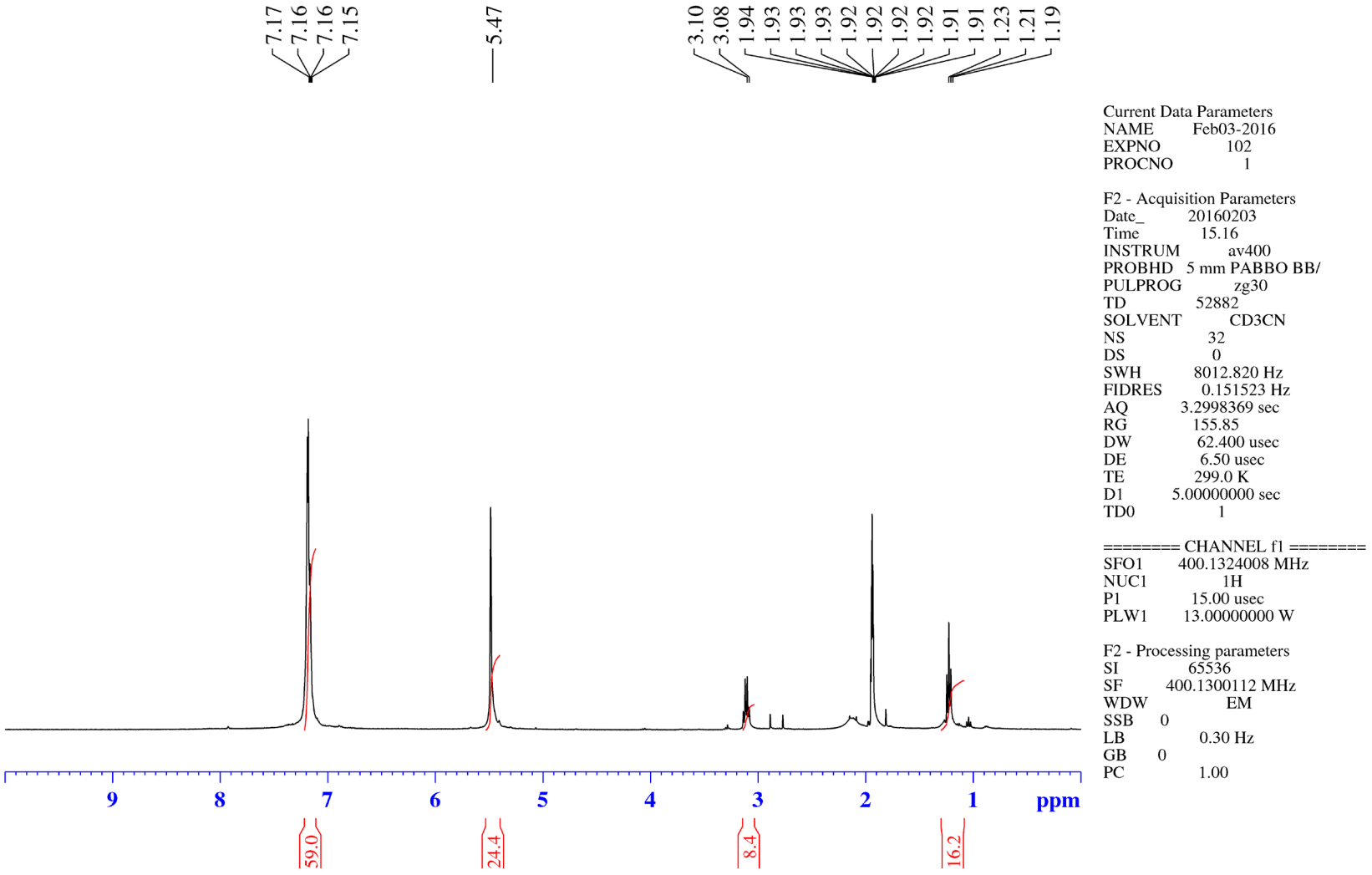
F2 - Acquisition Parameters
Date_ 20160129
Time 20.39
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

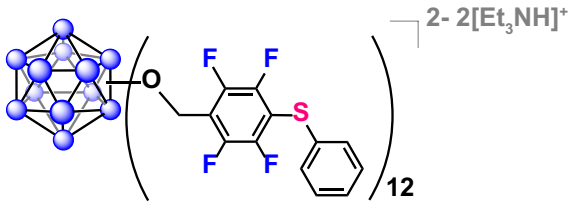


Current Data Parameters
NAME Feb03-2016
EXPNO 102
PROCNO 1

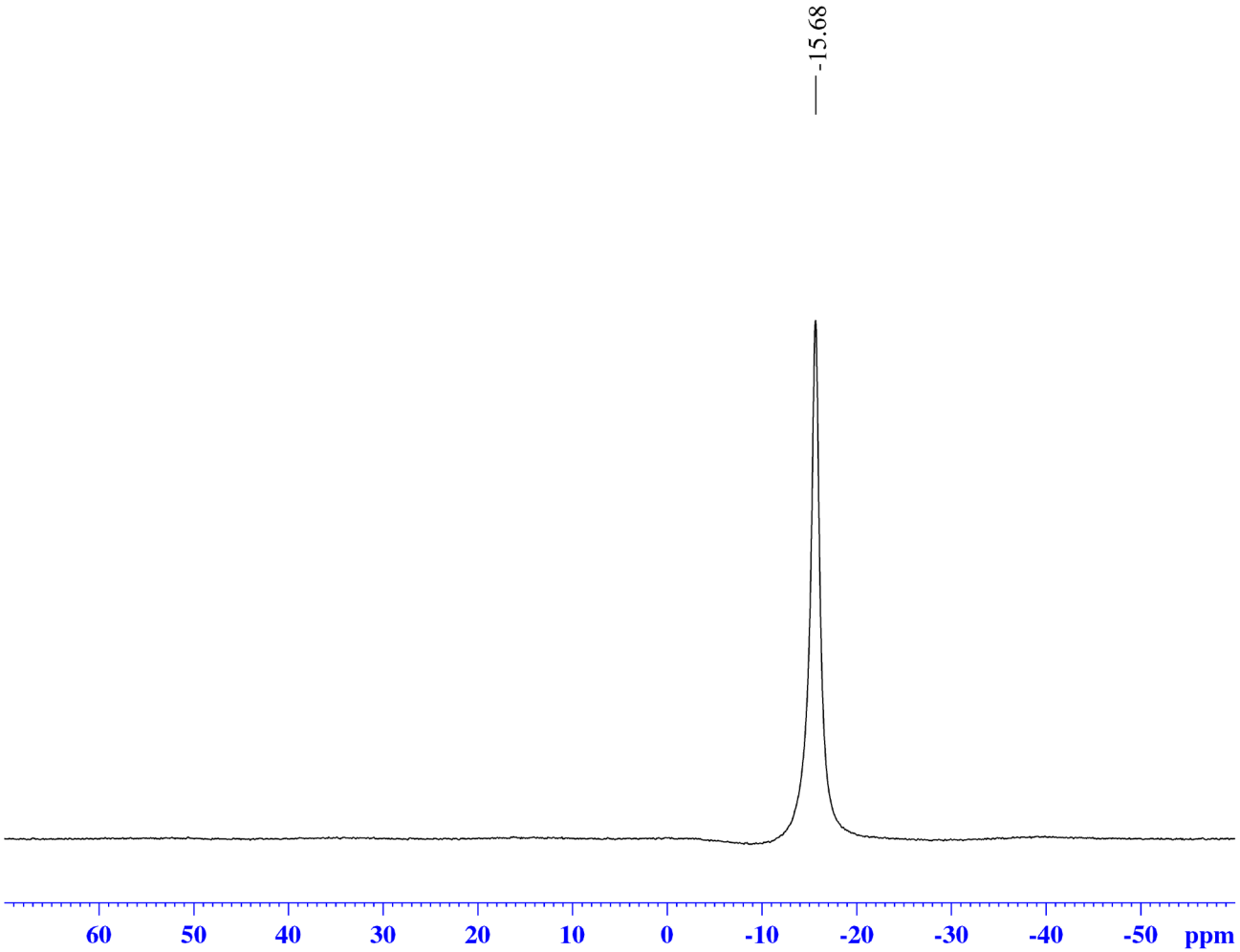
F2 - Acquisition Parameters
Date_ 20160203
Time 15.16
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CD3CN
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300112 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B {^{1}H} NMR



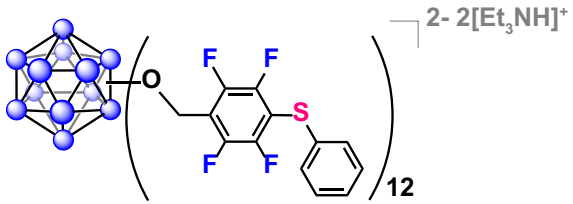
Current Data Parameters
NAME Feb03-2016
EXPNO 100
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160203
Time 15.06
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgdc.js
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

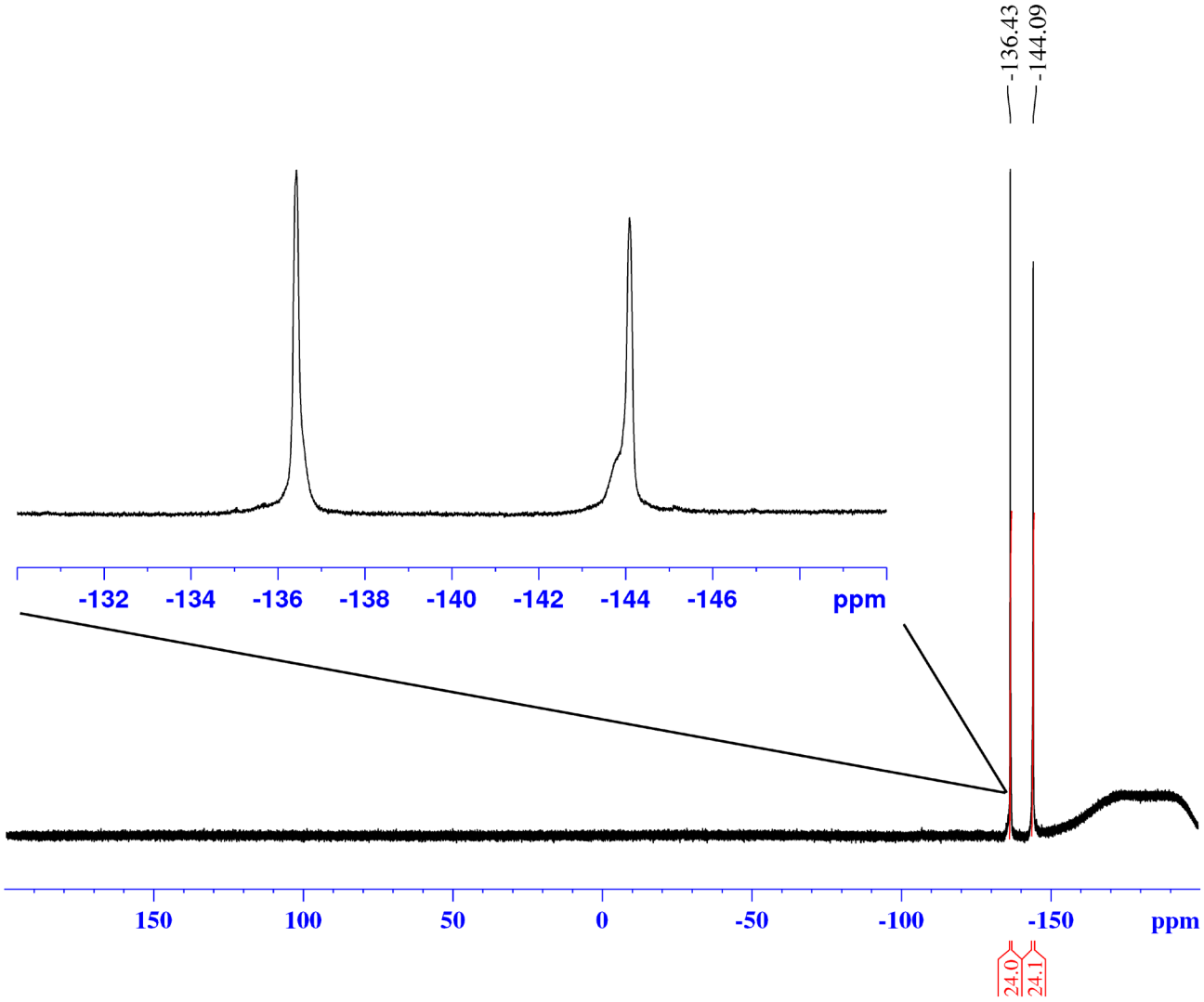
======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

BRUKER

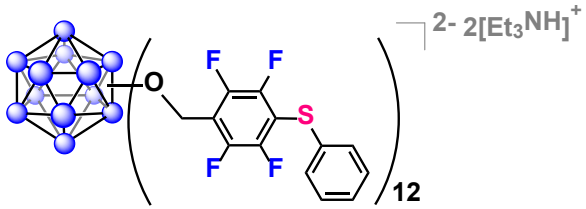


Current Data Parameters
NAME Feb03-2016
EXPNO 101
PROCNO 1

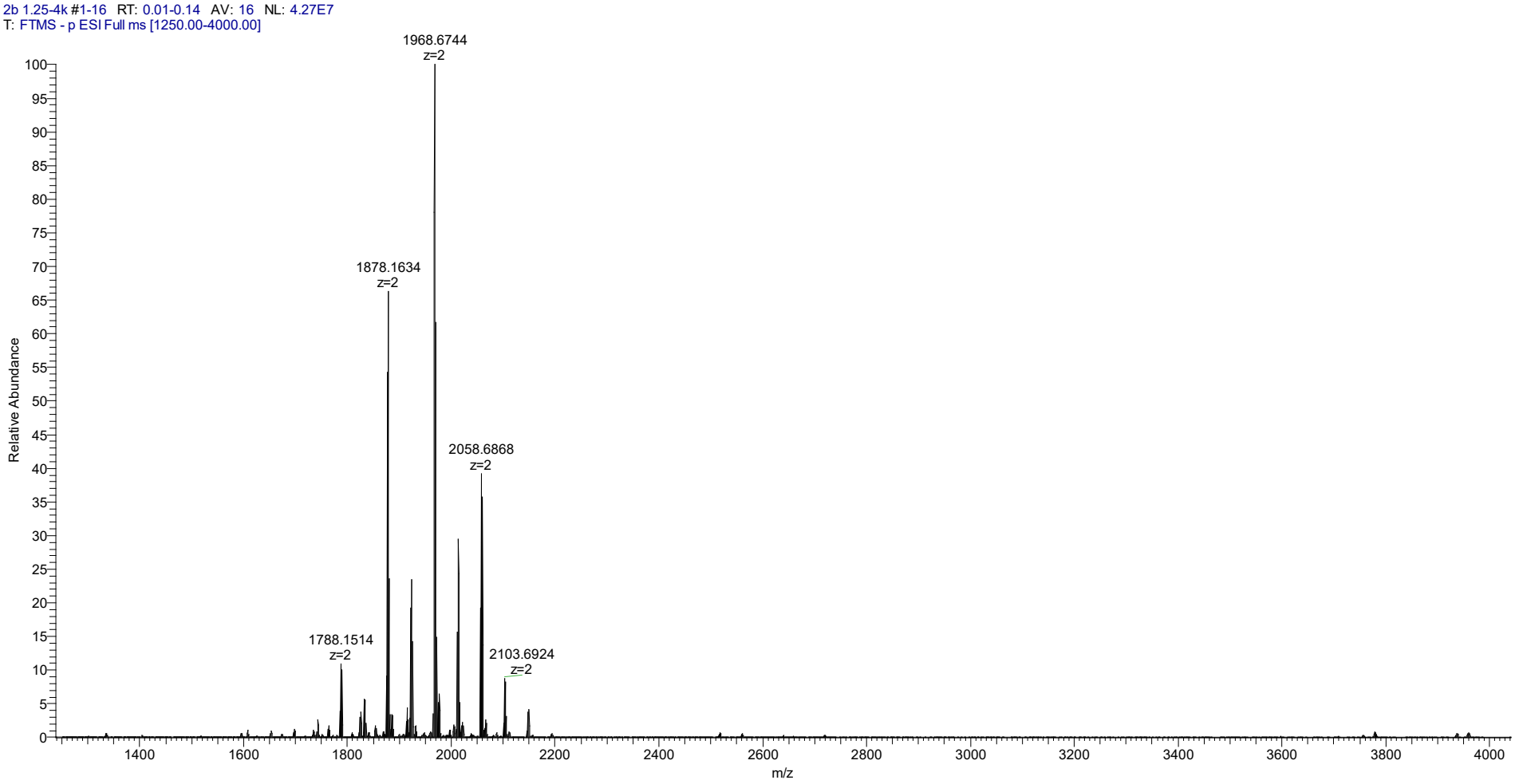
F2 - Acquisition Parameters
Date_ 20160203
Time 15.10
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

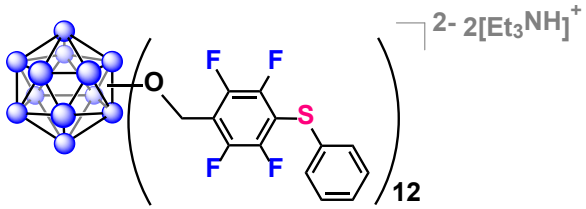
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

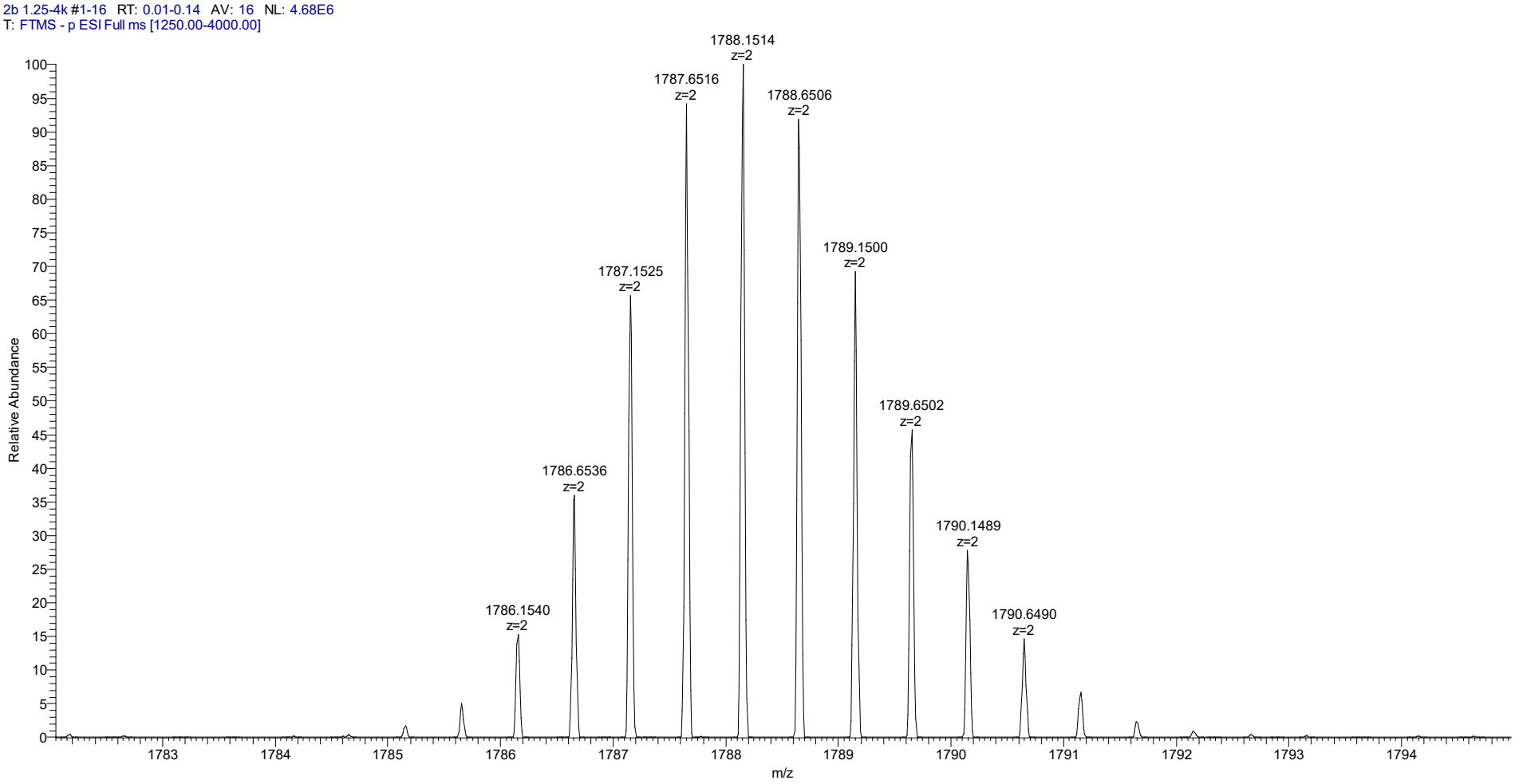


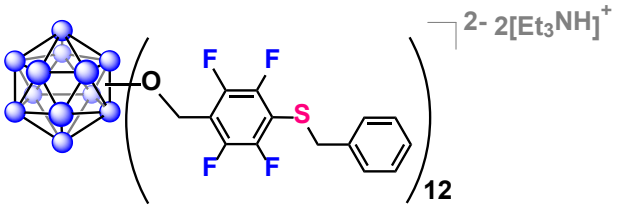
Q Exactive
High-Res Mass Spec



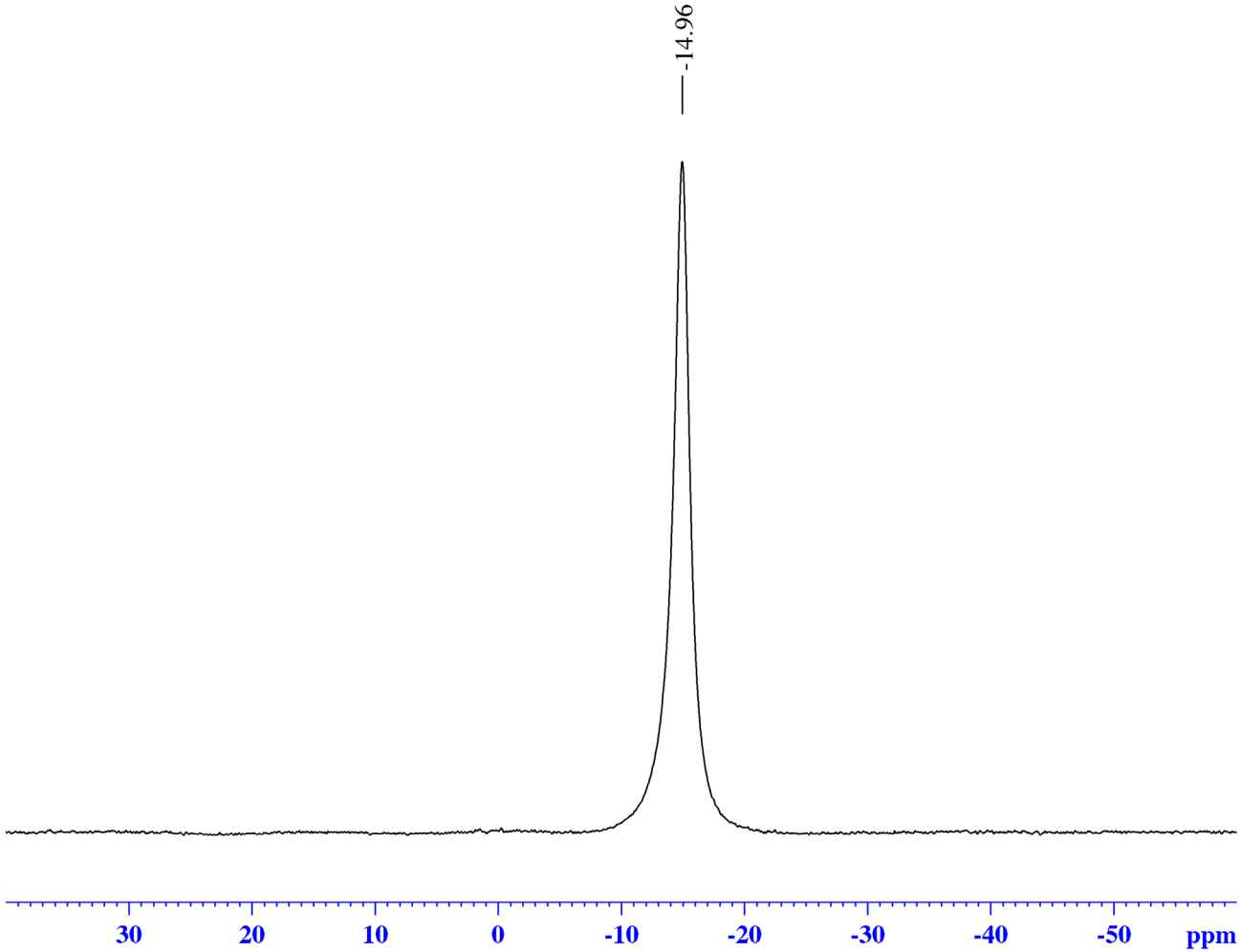


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

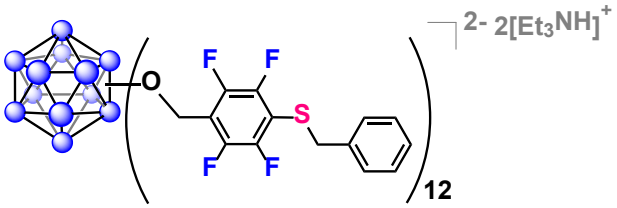


Current Data Parameters
NAME 0201
EXPNO 131
PROCNO 1

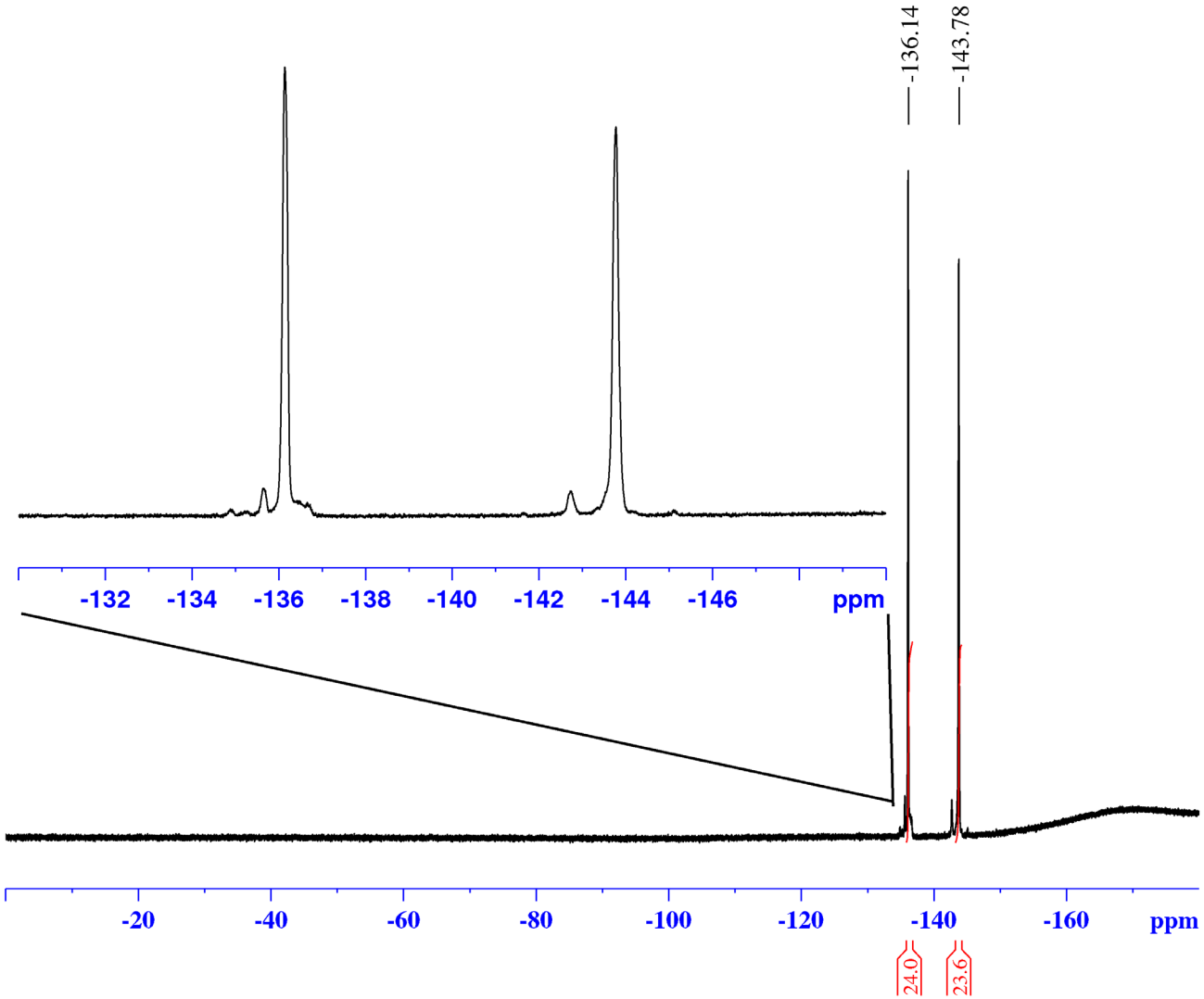
F2 - Acquisition Parameters
Date_ 20160201
Time 20.18
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

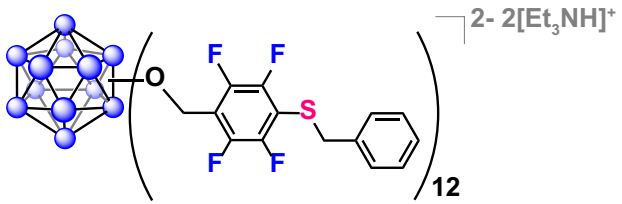


Current Data Parameters
NAME 0201
EXPNO 130
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160201
Time 20.15
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

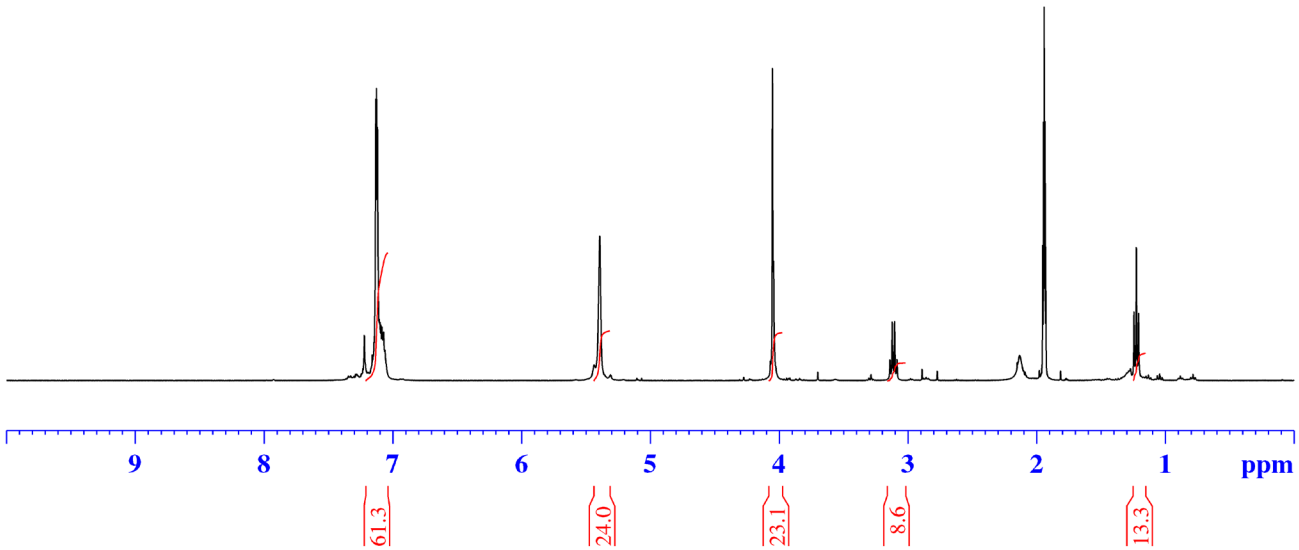
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

BRUKER

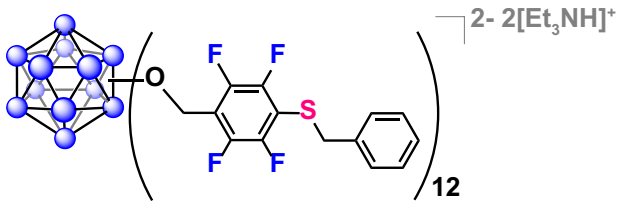


Current Data Parameters
NAME Feb03-2016
EXPNO 92
PROCNO 1

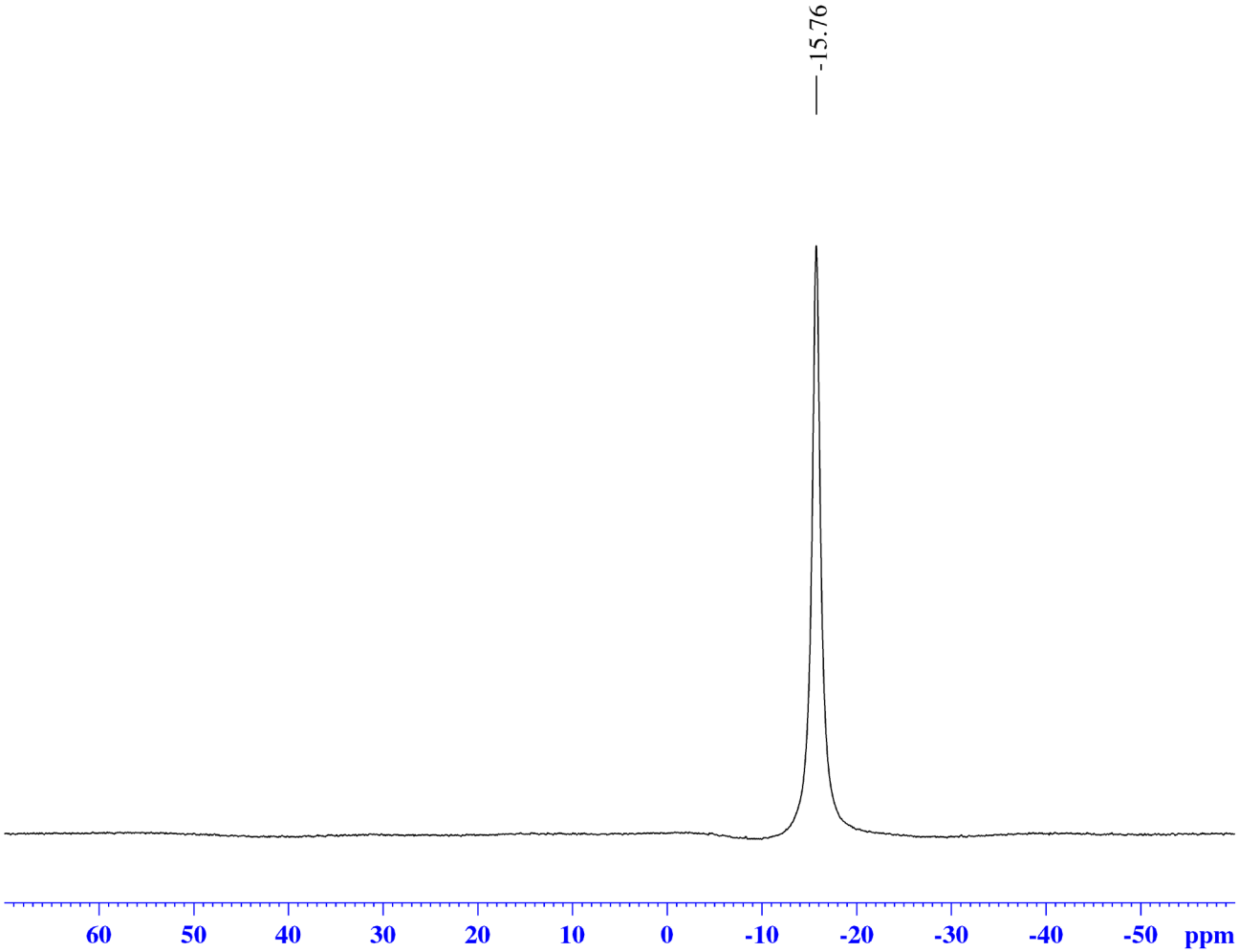
F2 - Acquisition Parameters
Date_ 20160203
Time 14.59
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CD3CN
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B {^{1}H} NMR



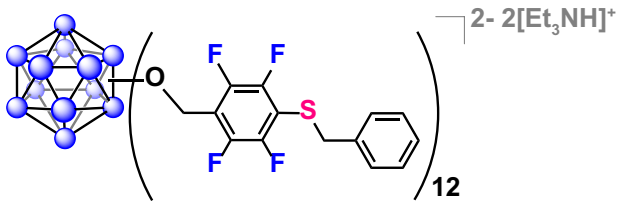
Current Data Parameters
NAME Feb03-2016
EXPNO 90
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160203
Time 14.49
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgdc.js
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
D11 0.03000000 sec
TD0 1

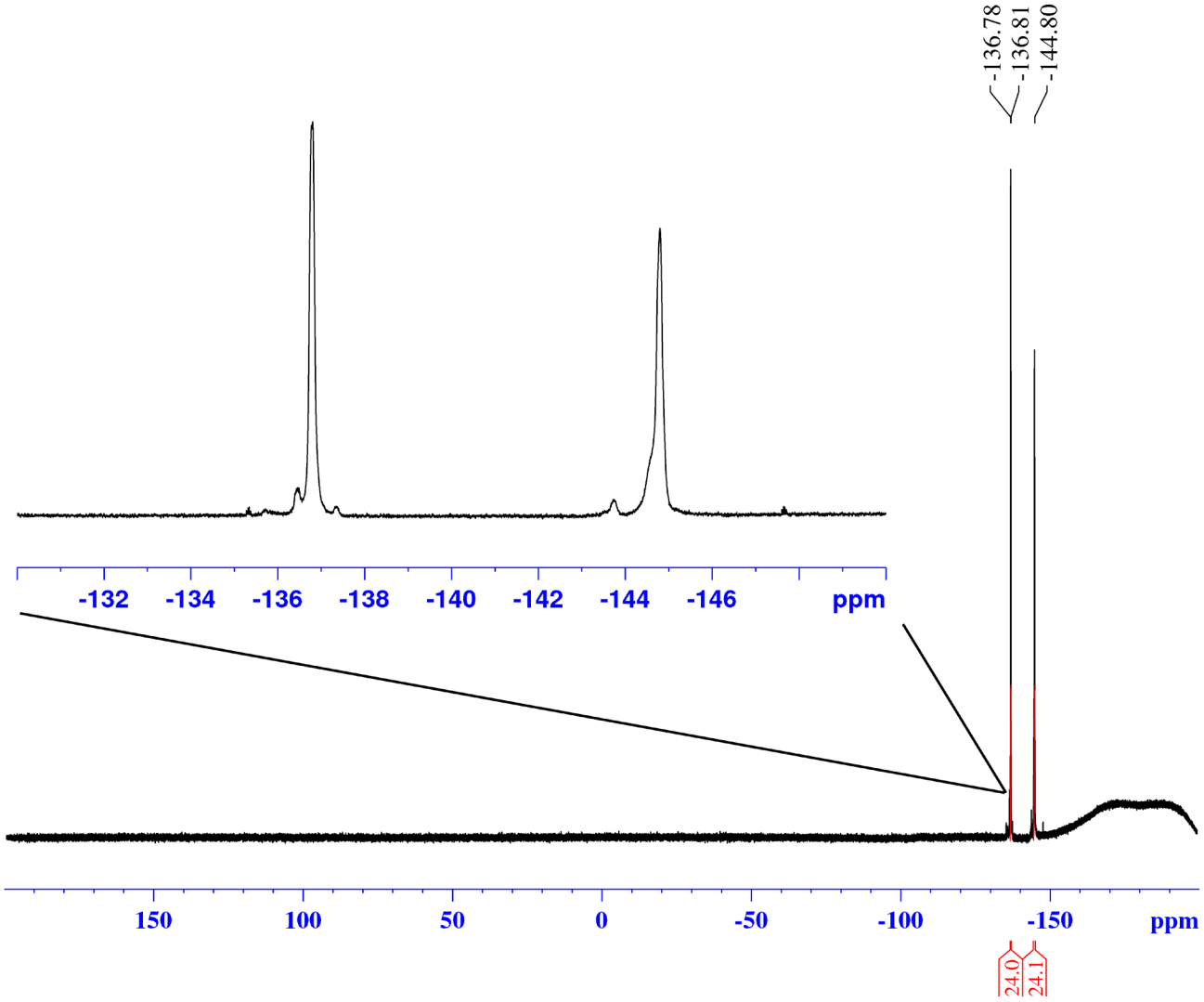
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

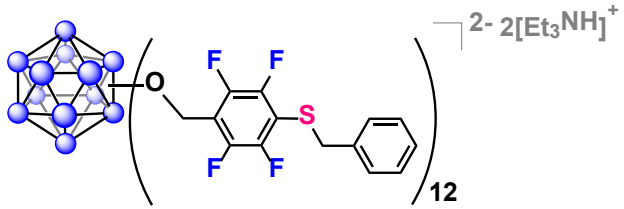


Current Data Parameters
NAME Feb03-2016
EXPNO 91
PROCNO 1

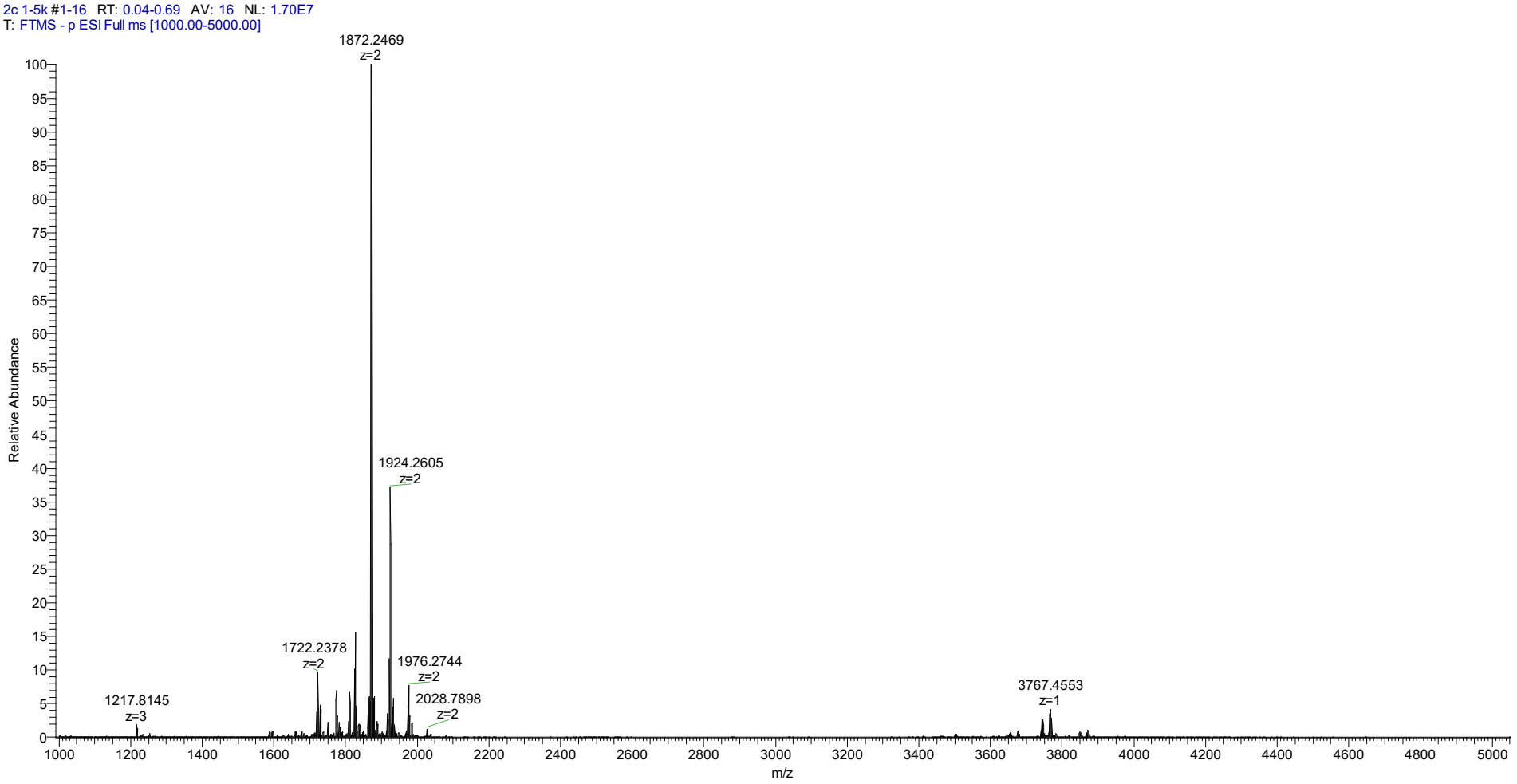
F2 - Acquisition Parameters
Date_ 20160203
Time 14.53
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

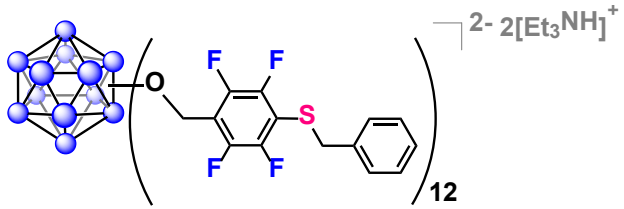
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

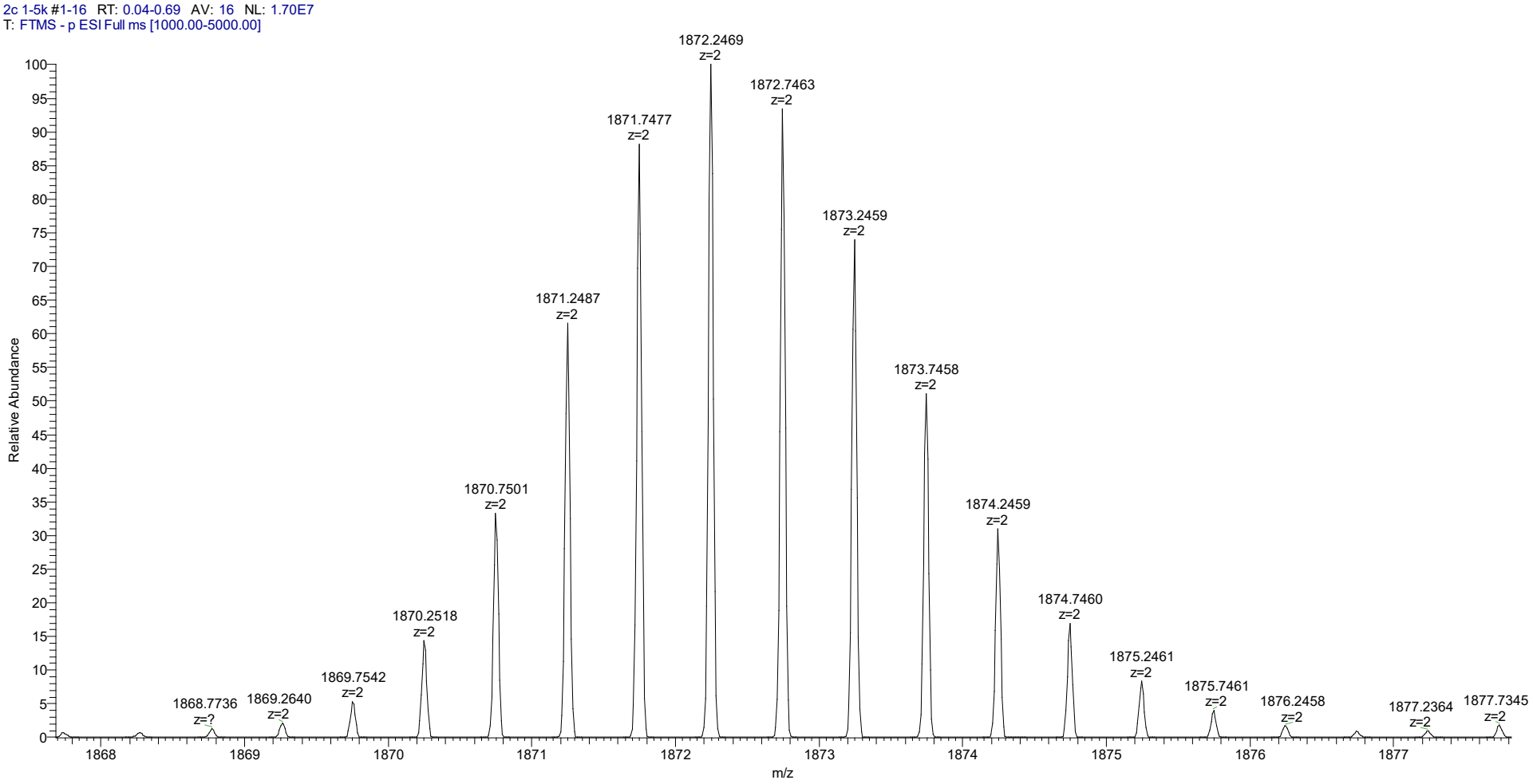


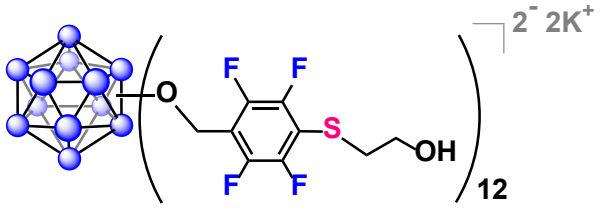
Q Exactive
High-Res Mass Spec



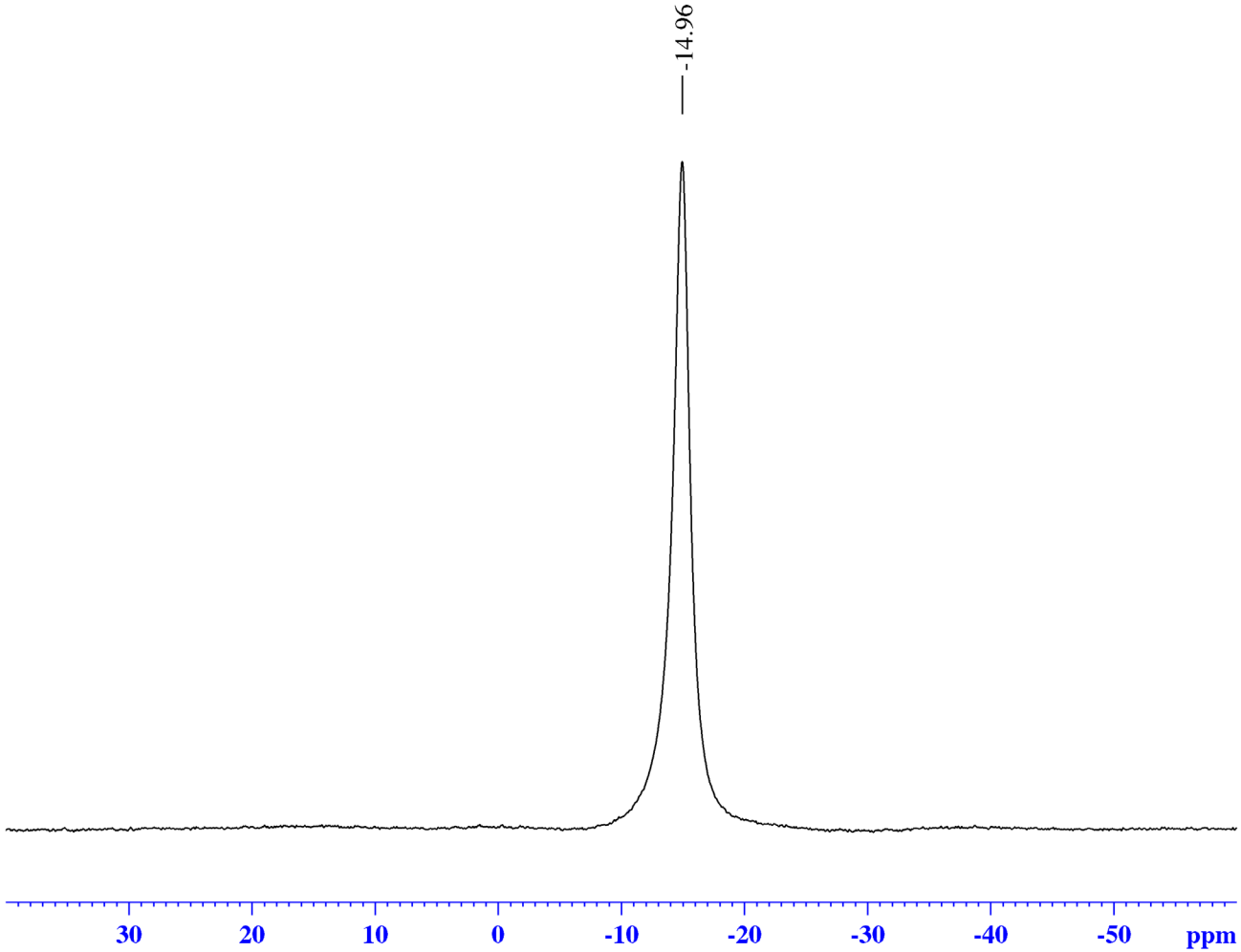


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

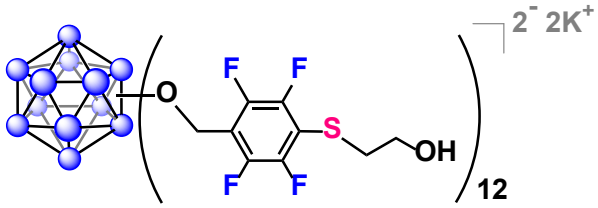


Current Data Parameters
NAME 0203
EXPNO 41
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160203
Time 13.16
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

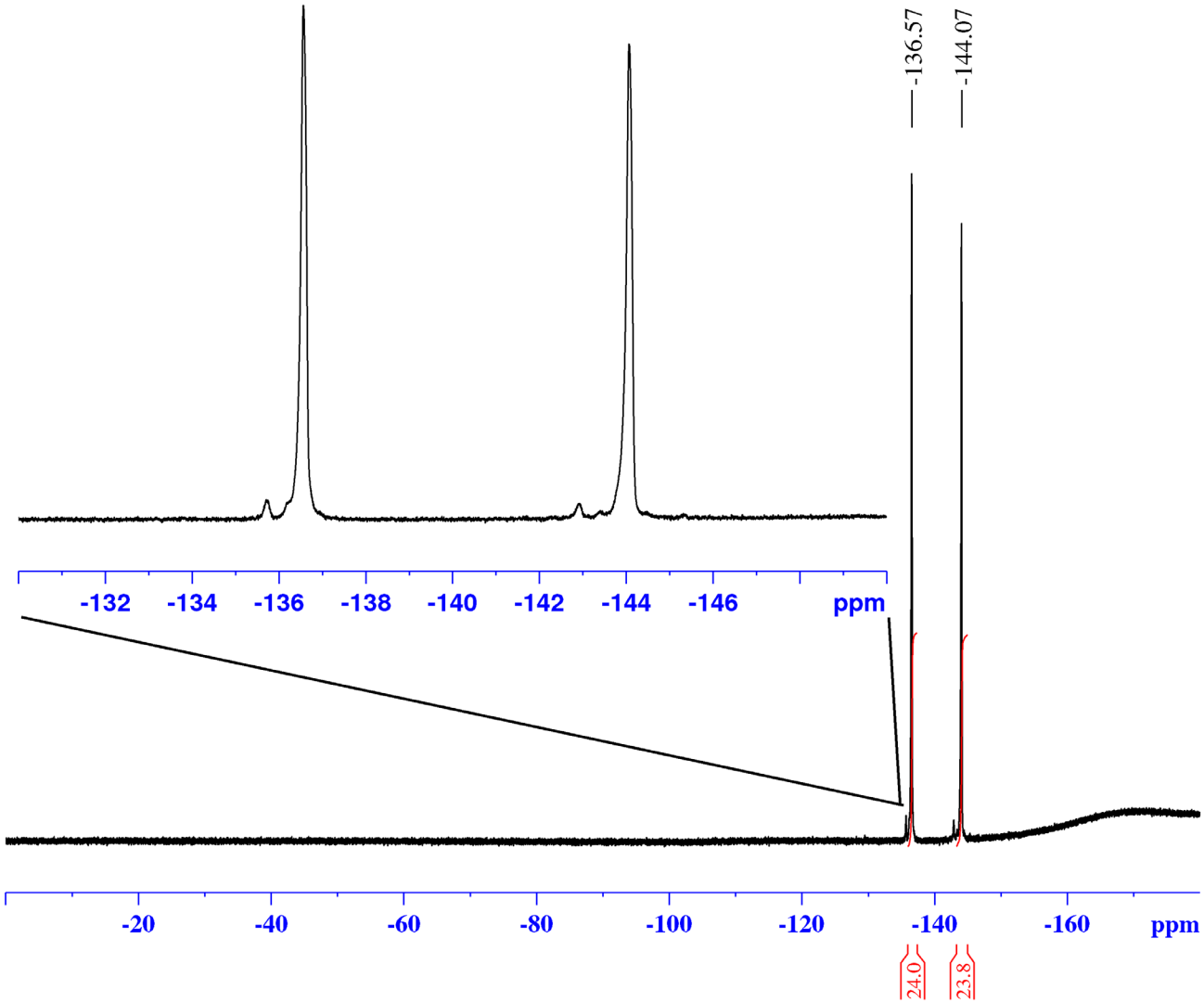
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

BRUKER

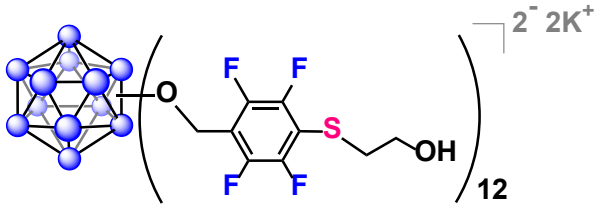


Current Data Parameters
NAME 0203
EXPNO 40
PROCNO 1

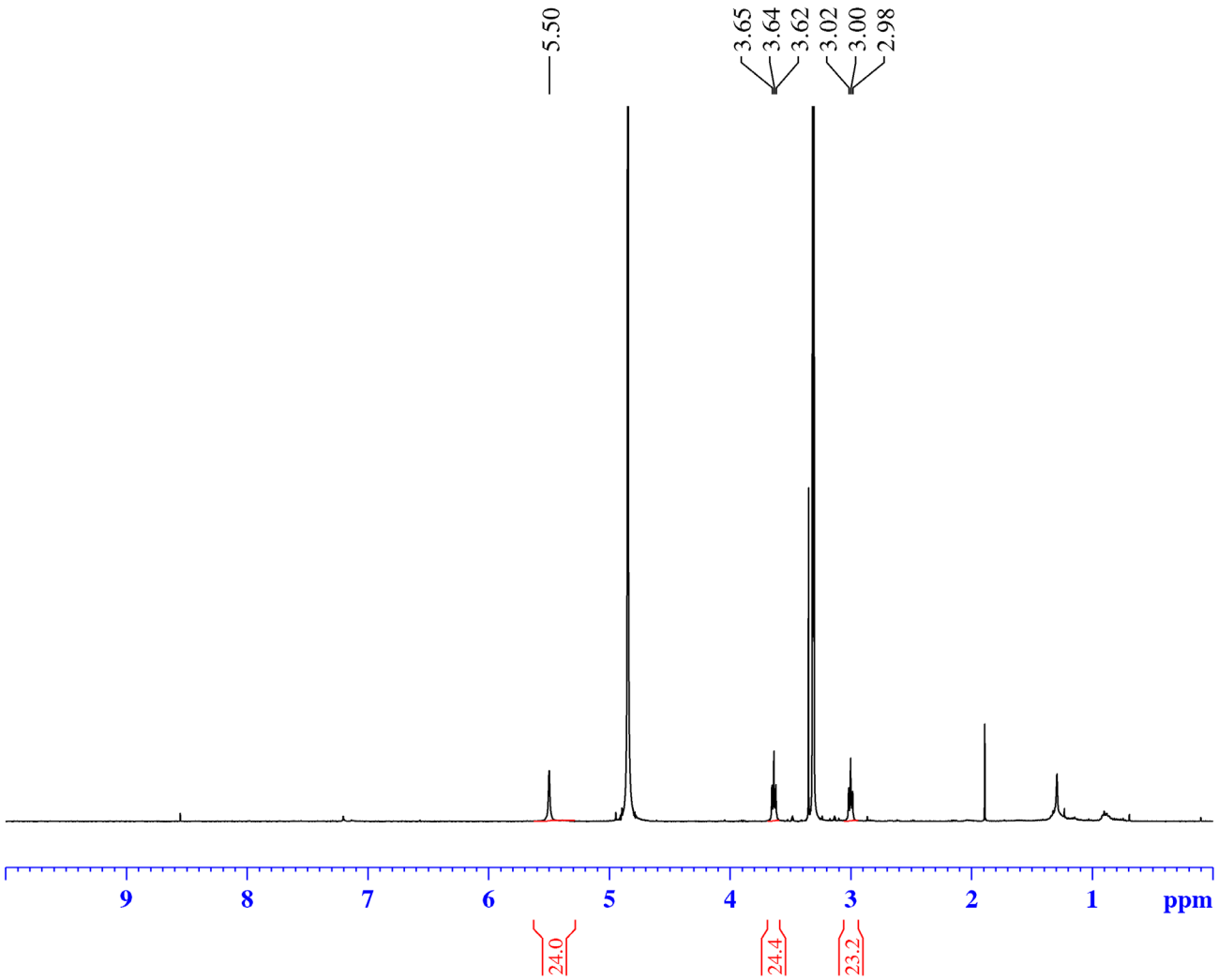
F2 - Acquisition Parameters
Date_ 20160203
Time 13.13
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

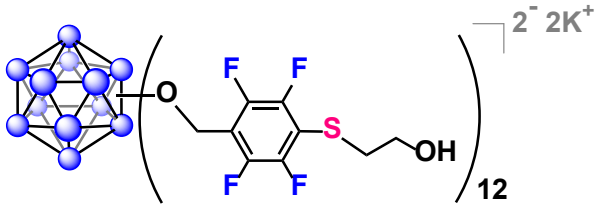


Current Data Parameters
NAME G1 2ME 0204 0202 (MeOD)
EXPNO 250
PROCNO 1

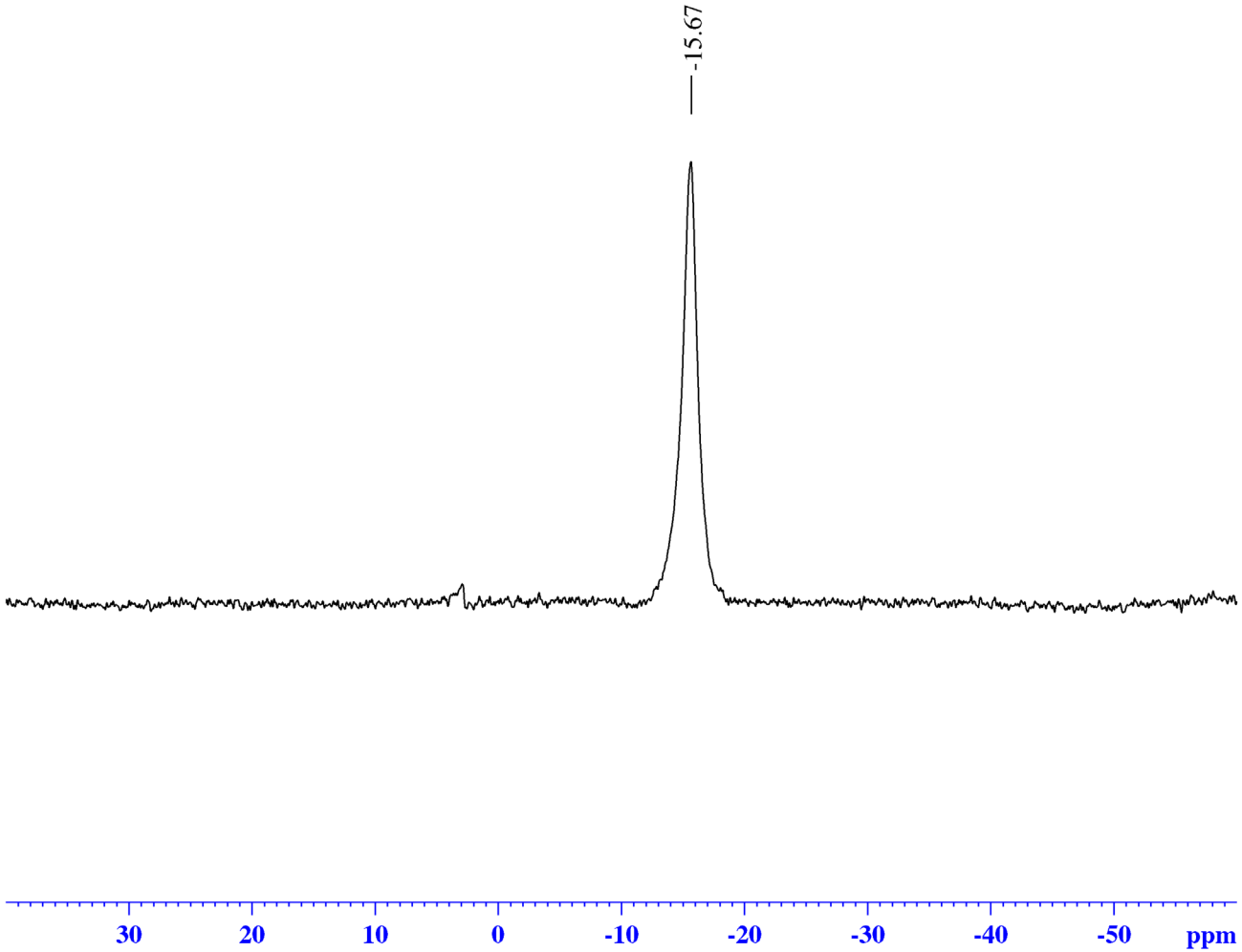
F2 - Acquisition Parameters
Date_ 20160208
Time 16.59
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

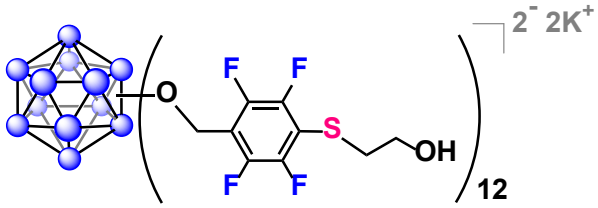


Current Data Parameters
NAME G1 2ME 0204 0202 (MeOD)
EXPNO 251
PROCNO 1

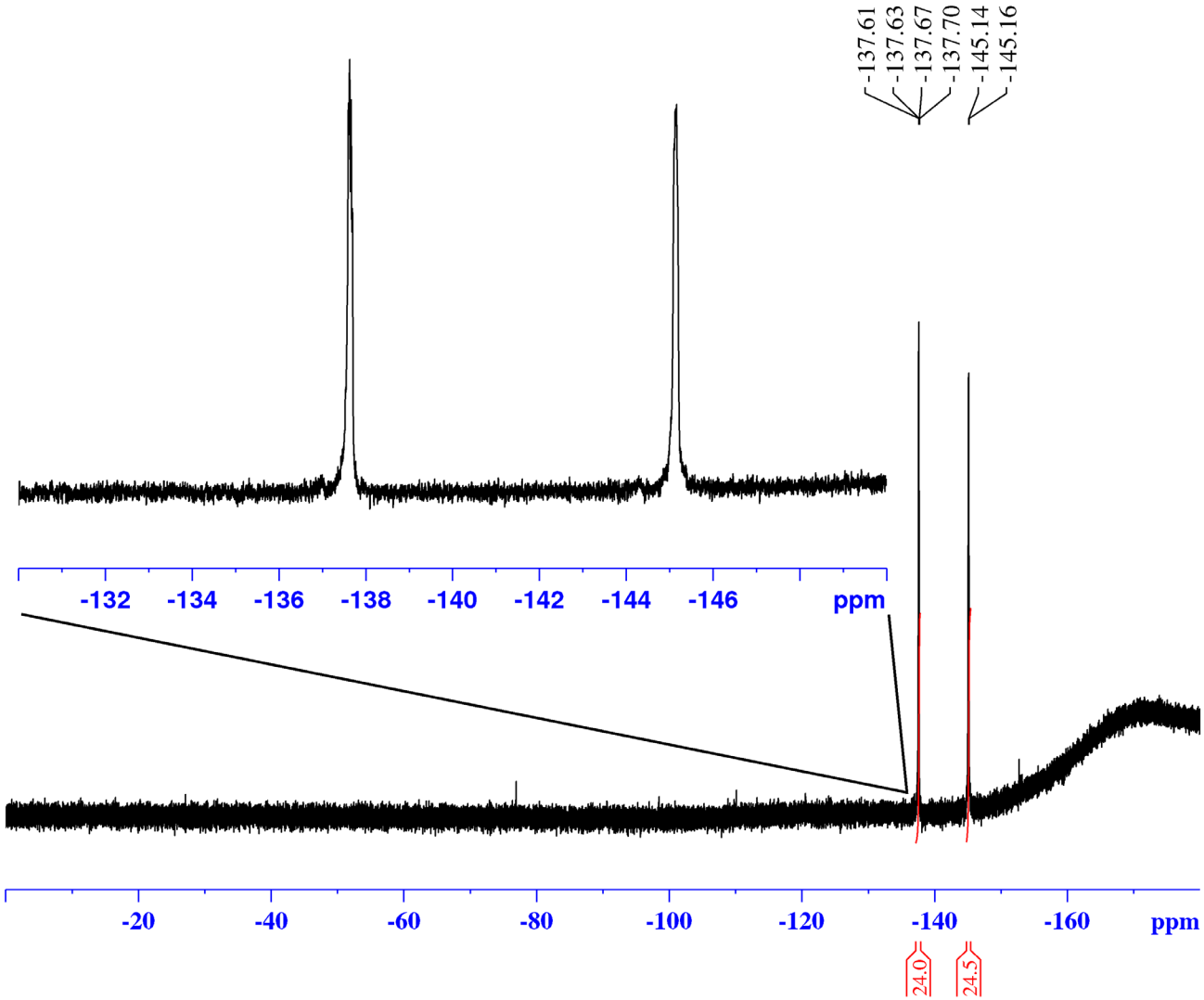
F2 - Acquisition Parameters
Date_ 20160208
Time 17.02
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

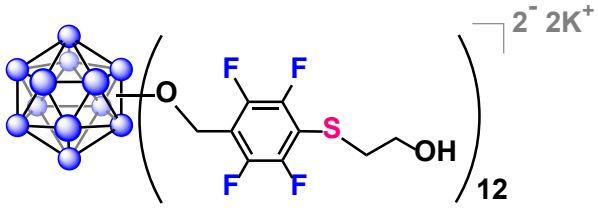


Current Data Parameters
NAME G1 2ME 0204 0202 (MeOD)
EXPNO 252
PROCNO 1

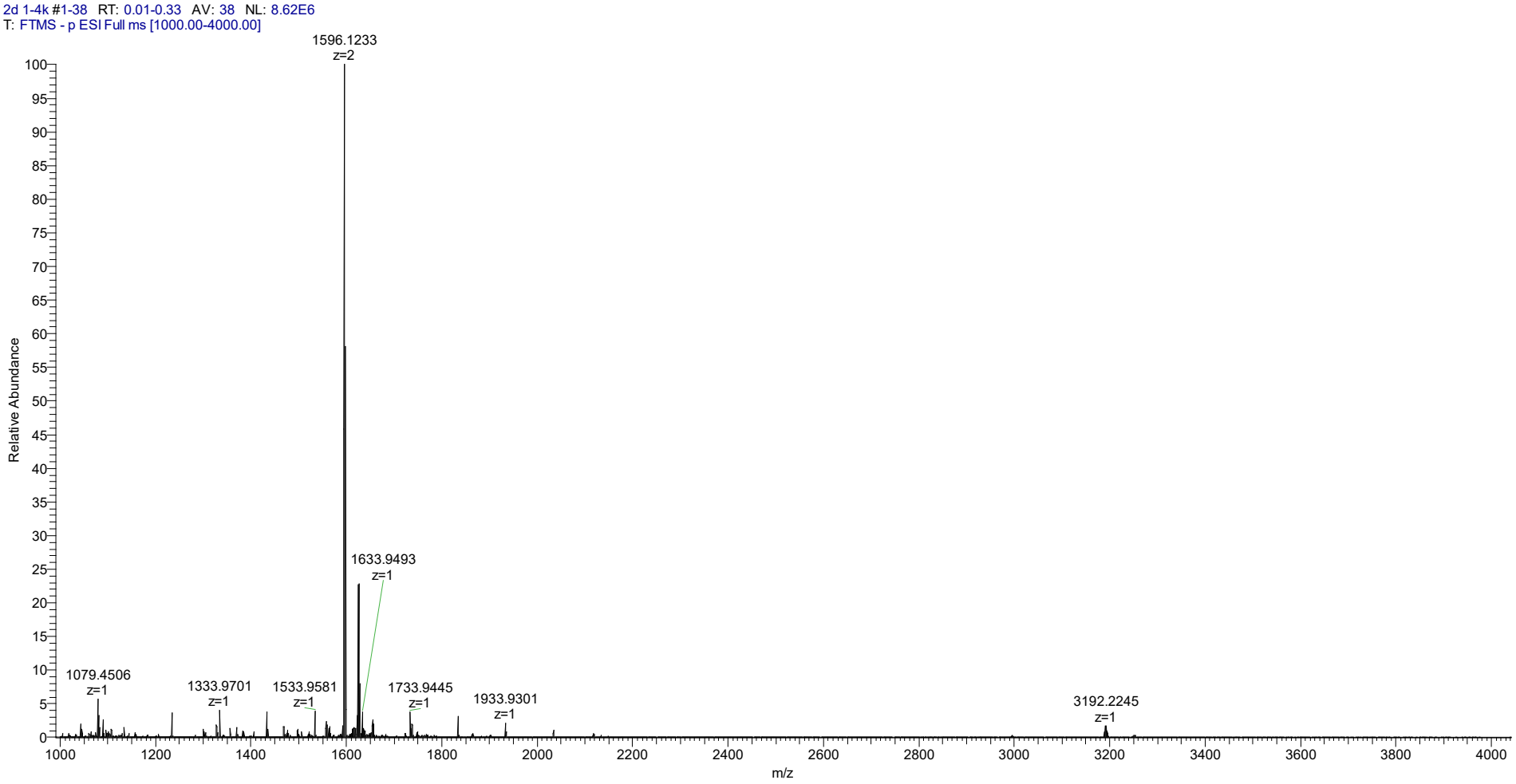
F2 - Acquisition Parameters
Date_ 20160208
Time 17.06
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

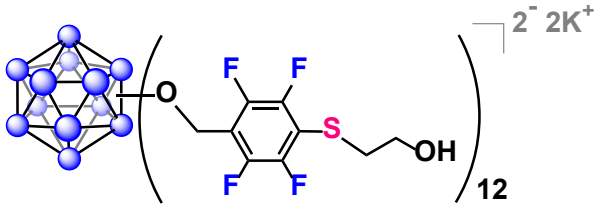
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

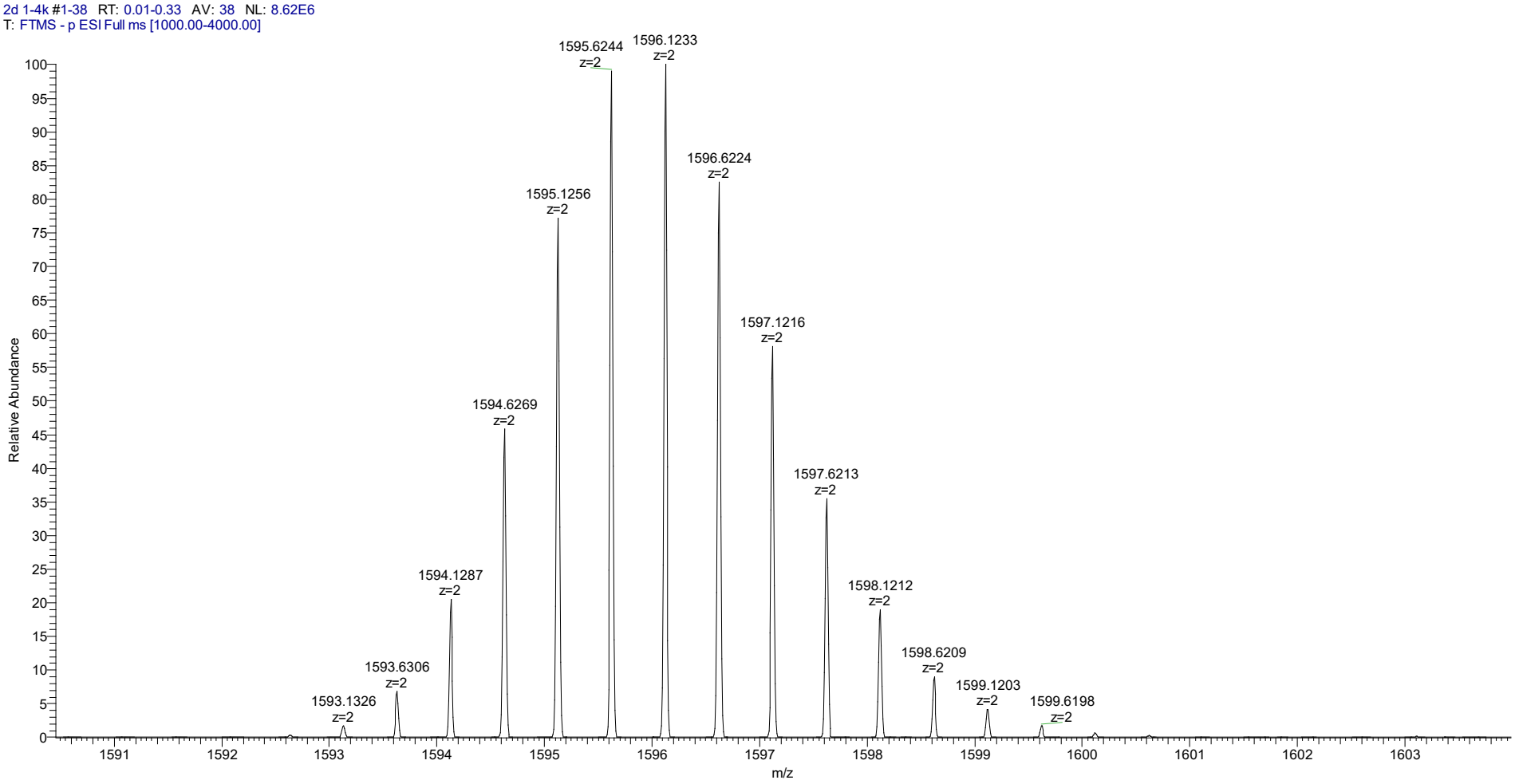


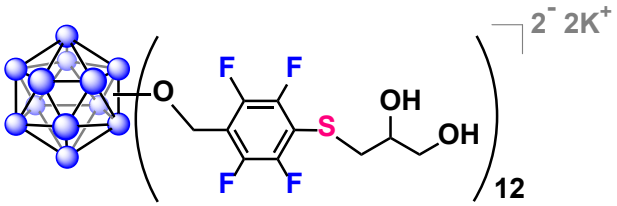
Q Exactive
High-Res Mass Spec



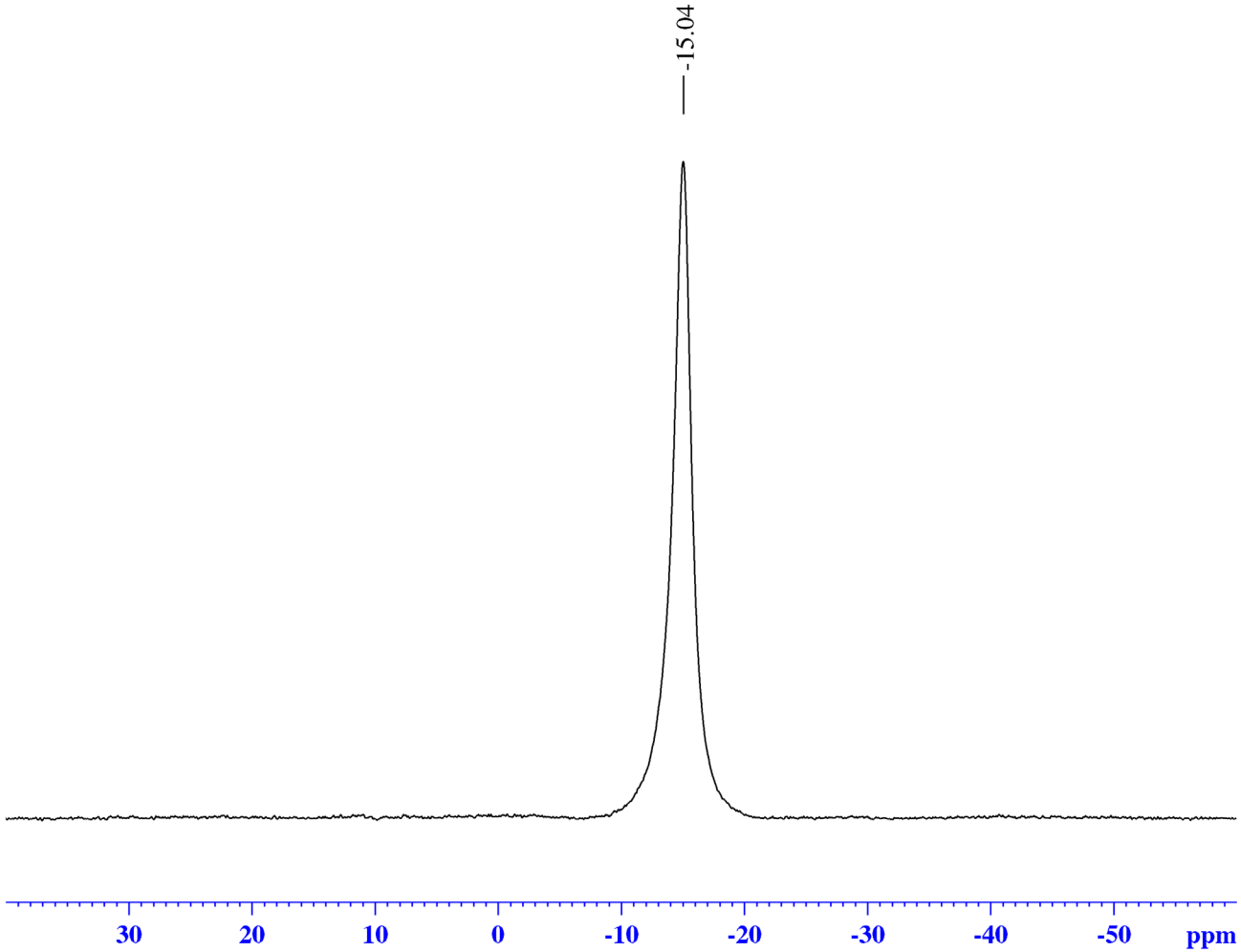


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

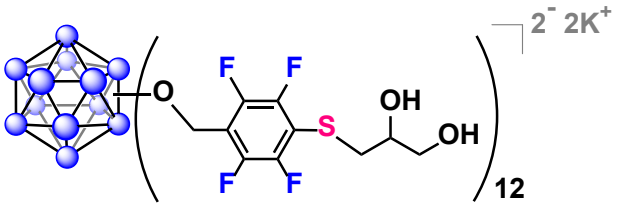


Current Data Parameters
NAME 0203
EXPNO 51
PROCNO 1

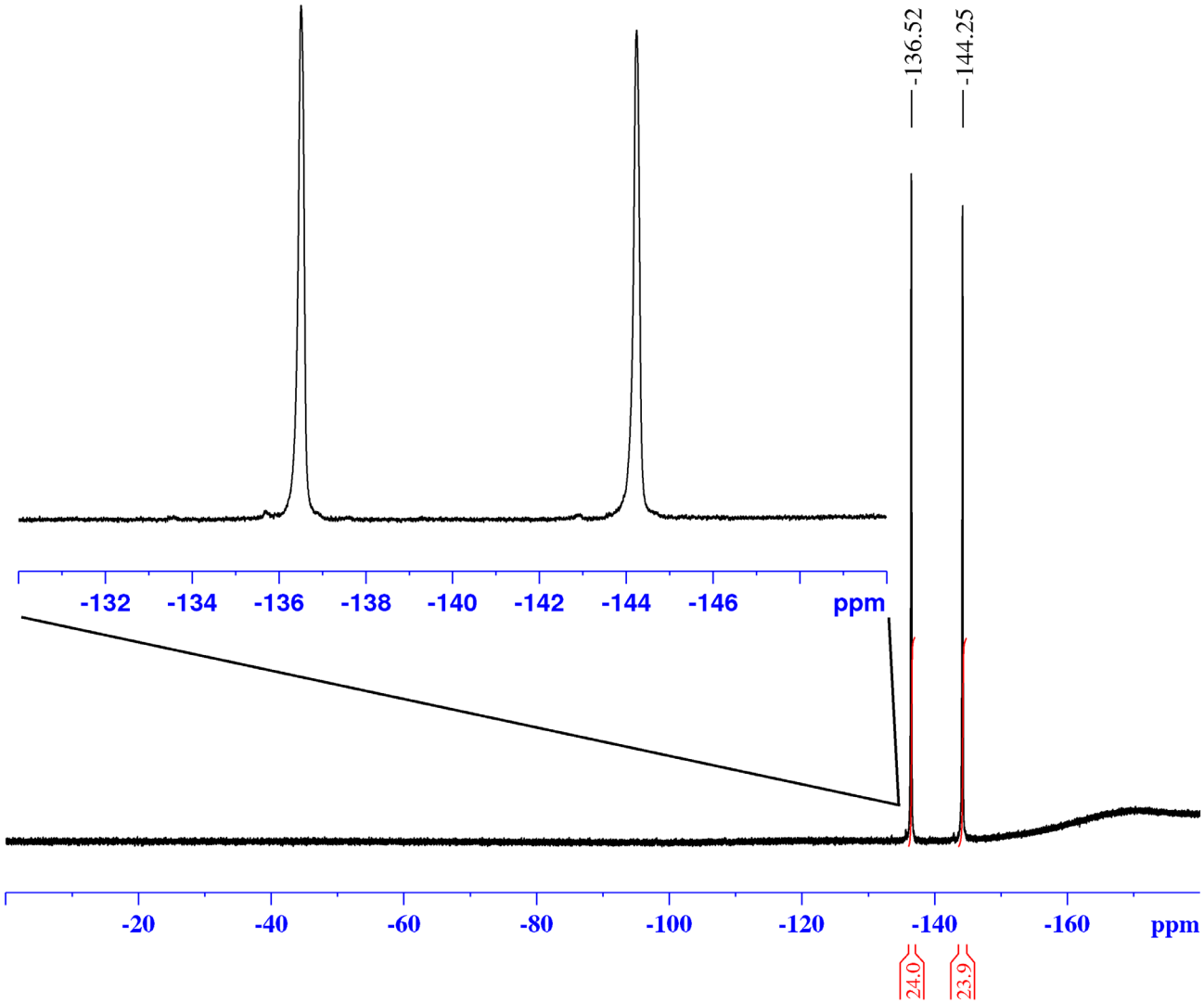
F2 - Acquisition Parameters
Date_ 20160203
Time 13.25
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

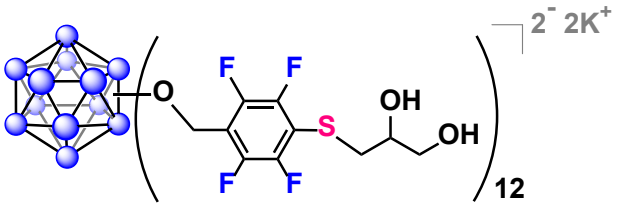


Current Data Parameters
NAME 0203
EXPNO 50
PROCNO 1

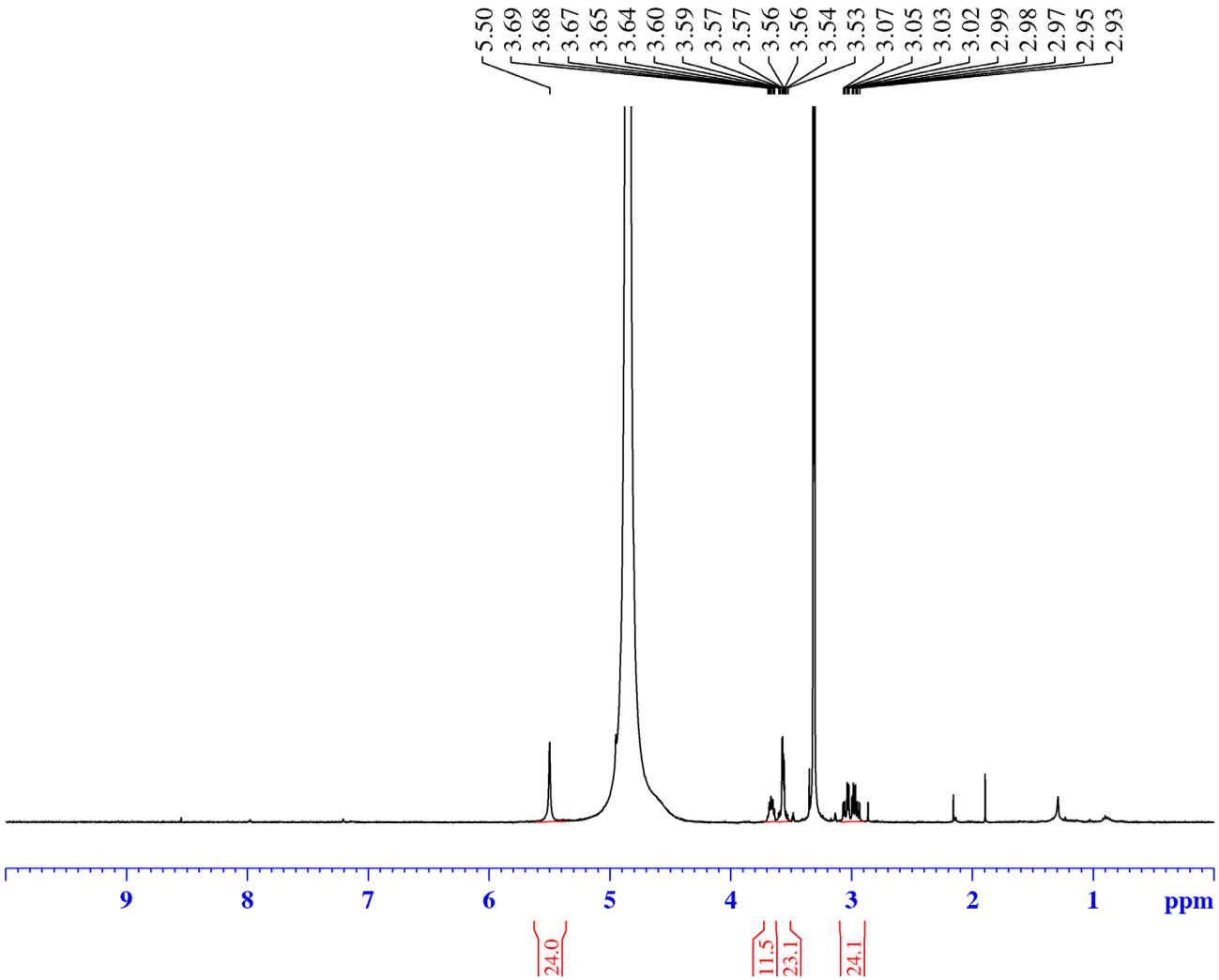
F2 - Acquisition Parameters
Date_ 20160203
Time 13.22
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

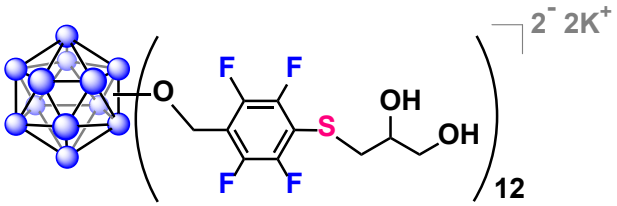


Current Data Parameters
NAME G1 Glycerol 0204 0202 (MeOD)
EXPNO 90
PROCNO 1

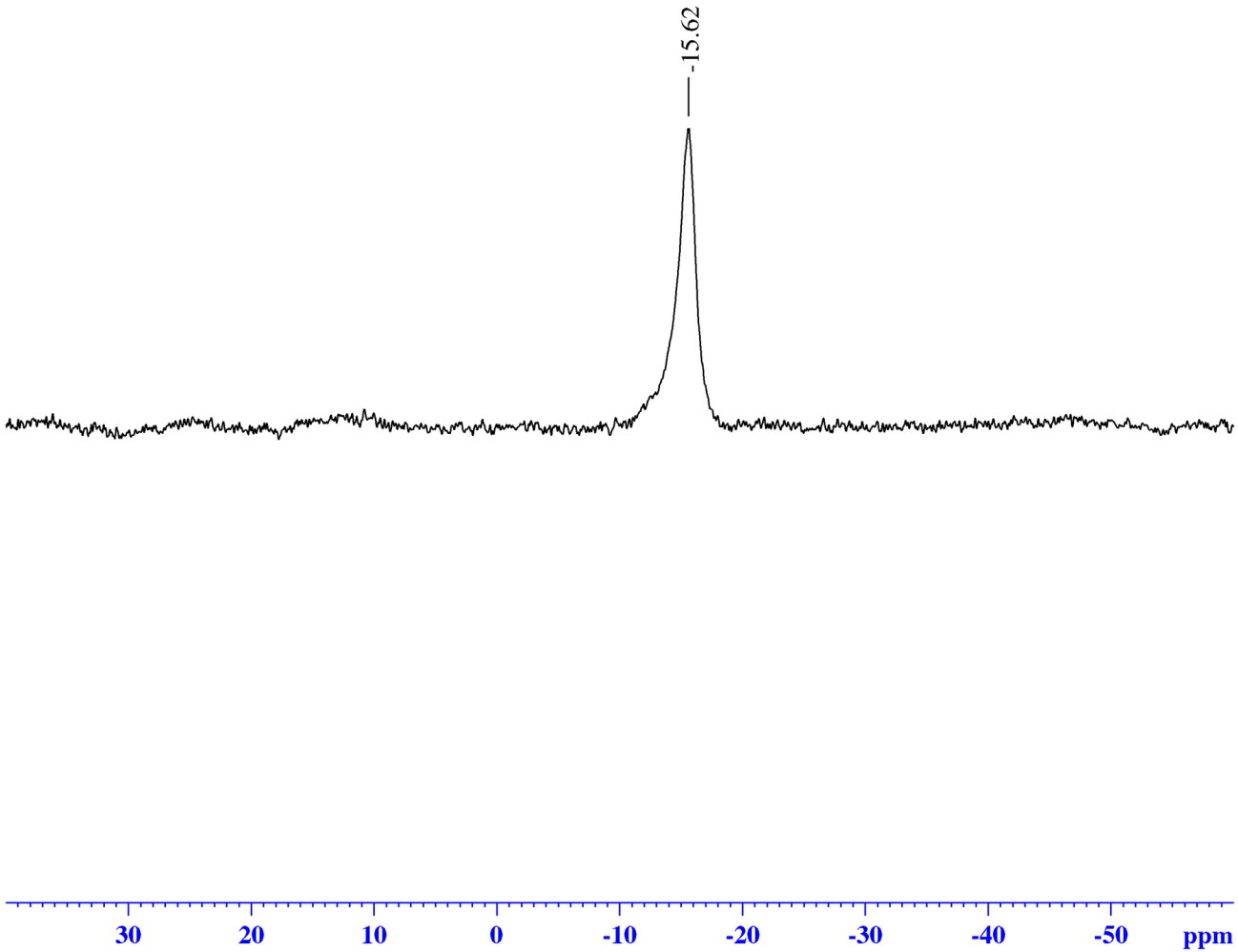
F2 - Acquisition Parameters
Date_ 20160205
Time 12.37
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

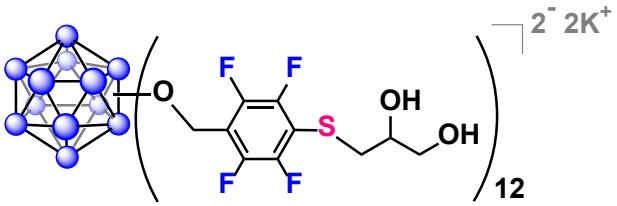


Current Data Parameters
NAME G1 Glycerol 0204 0202 (MeOD)
EXPNO 91
PROCNO 1

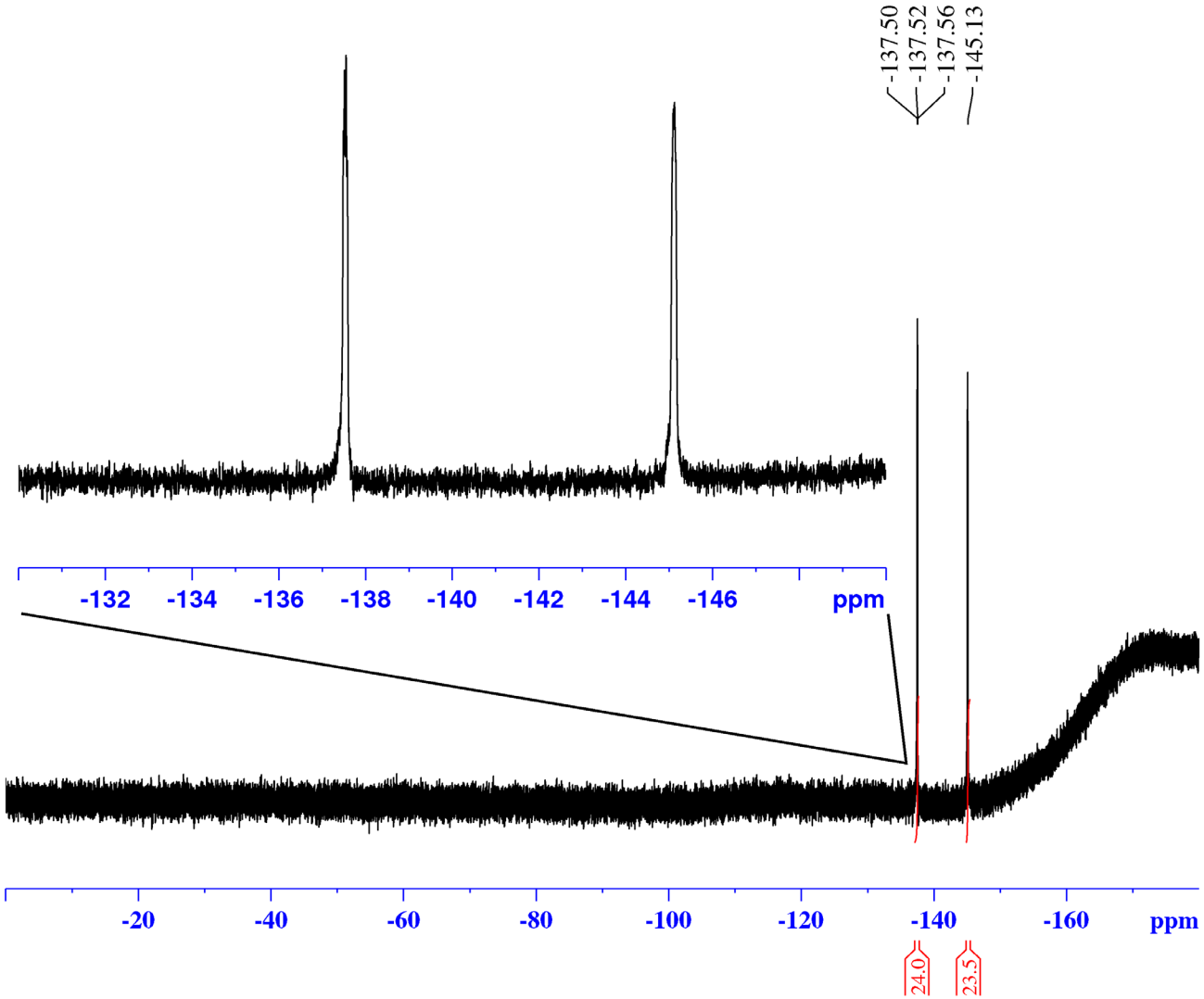
F2 - Acquisition Parameters
Date_ 20160205
Time 12.40
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

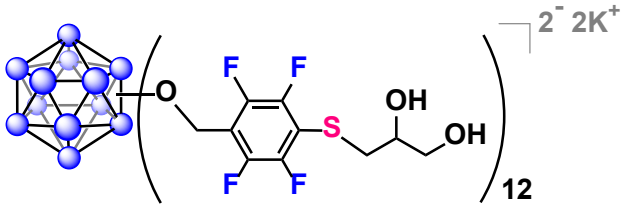


Current Data Parameters
NAME G1 Glycerol 0204 0202 (MeOD)
EXPNO 92
PROCNO 1

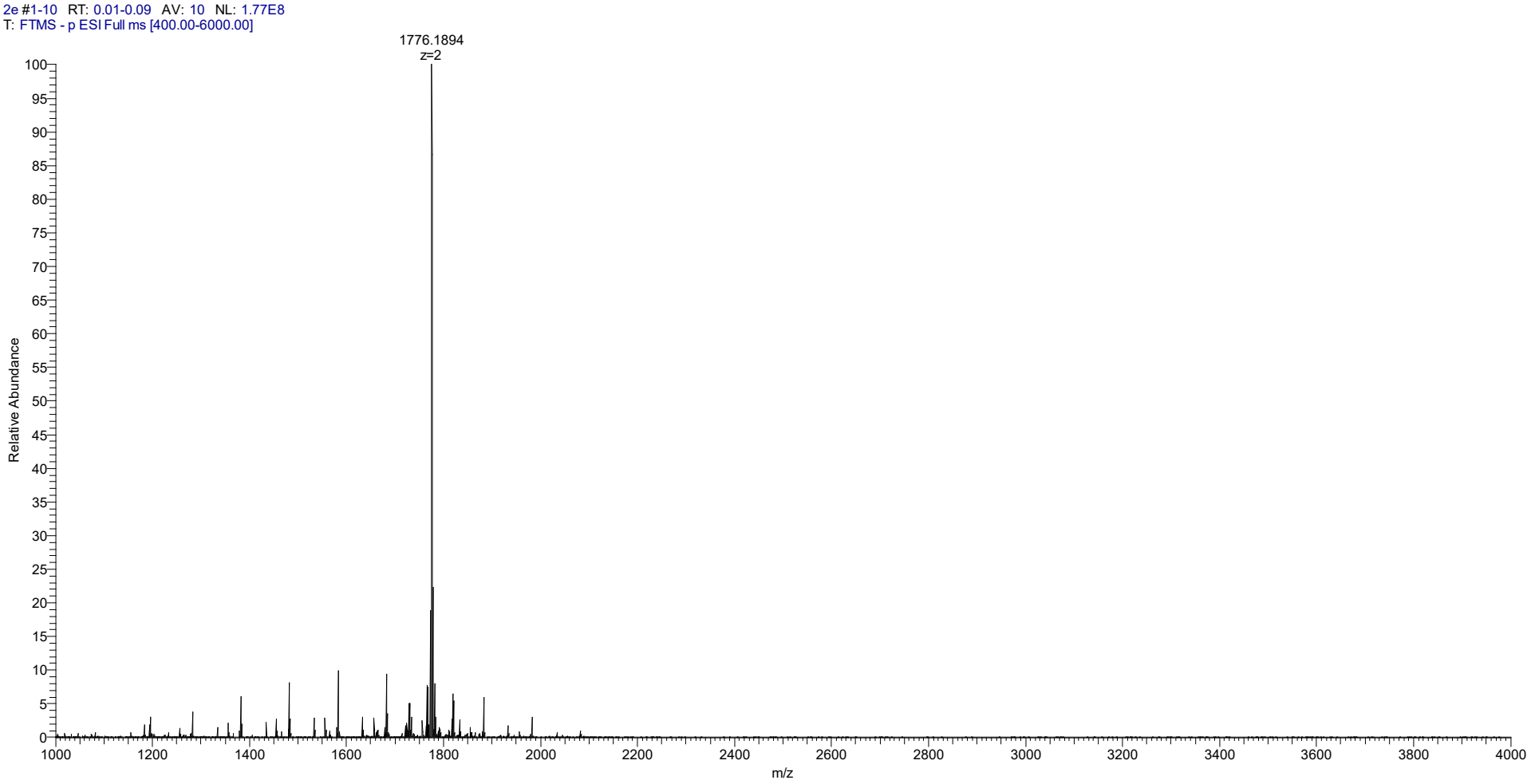
F2 - Acquisition Parameters
Date_ 20160205
Time 12.45
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

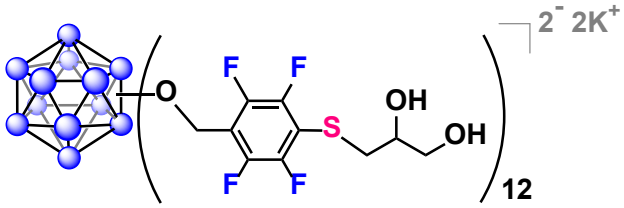
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

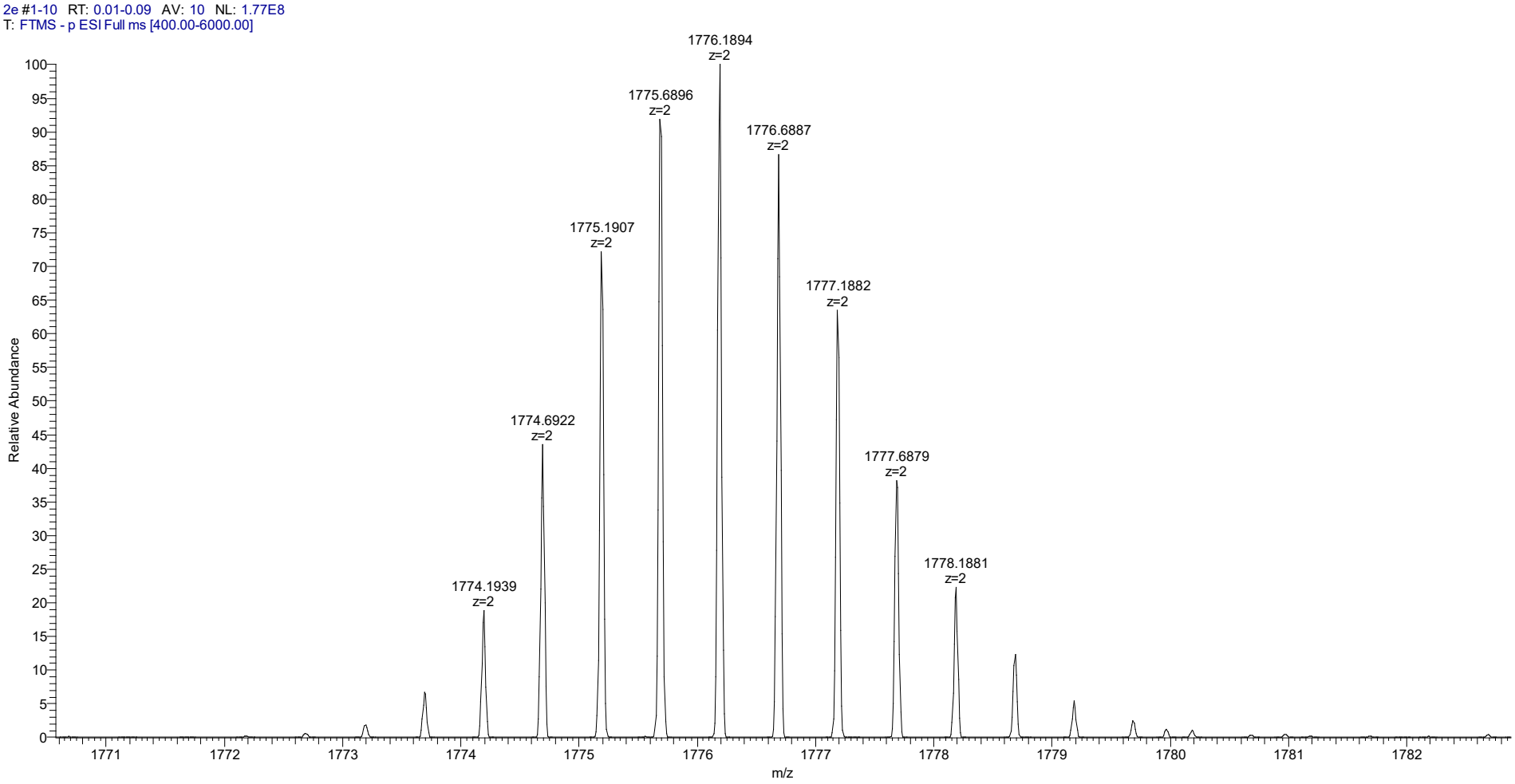


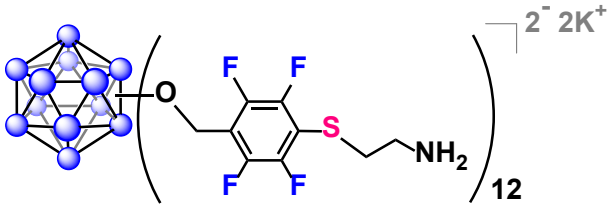
Q Exactive
High-Res Mass Spec



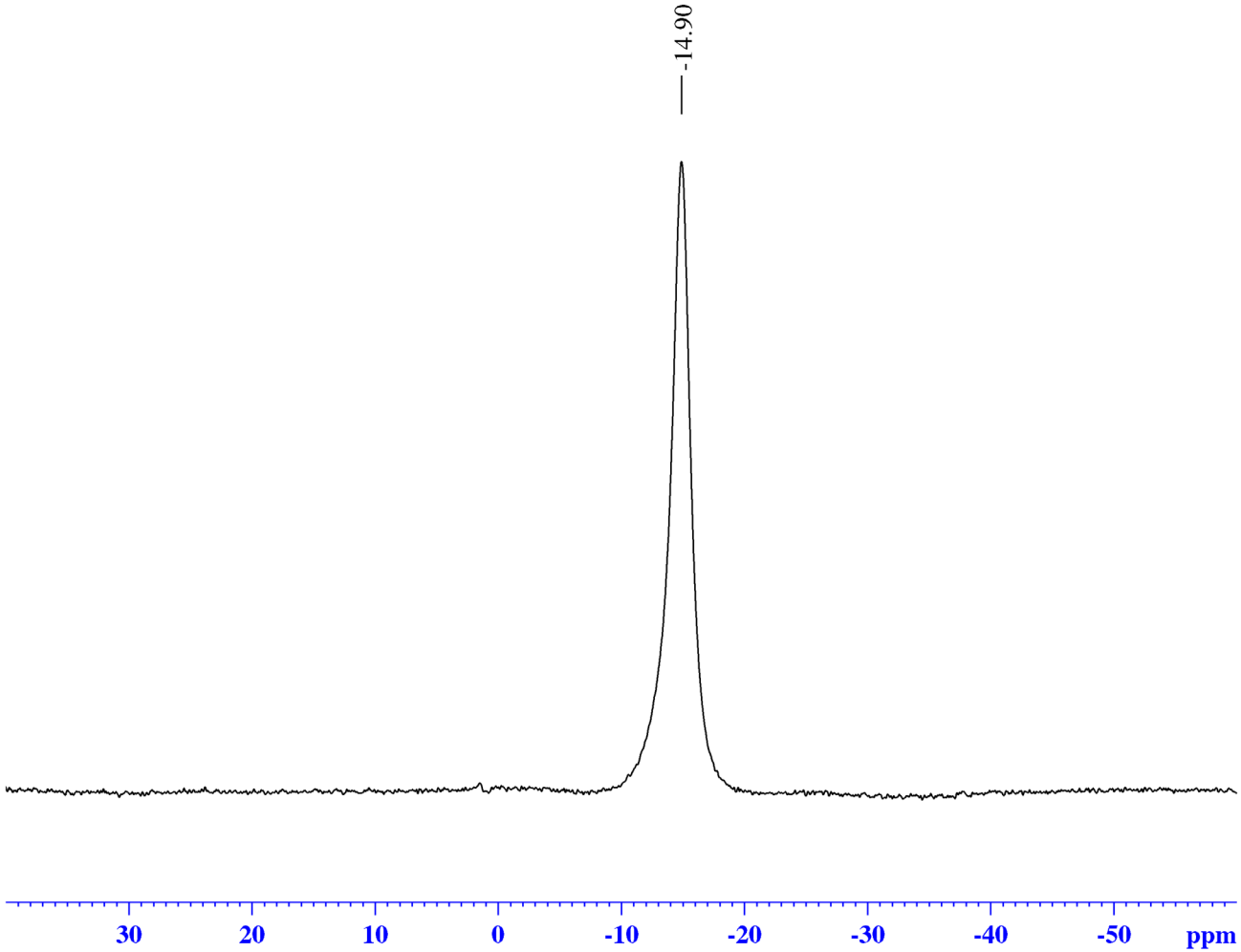


Q Exactive
High-Res Mass Spec





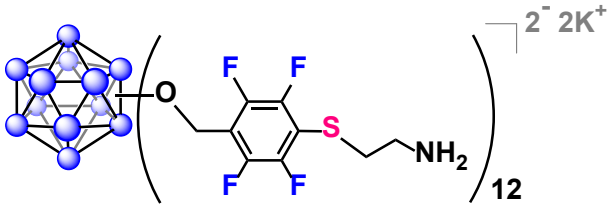
in situ ^{11}B NMR



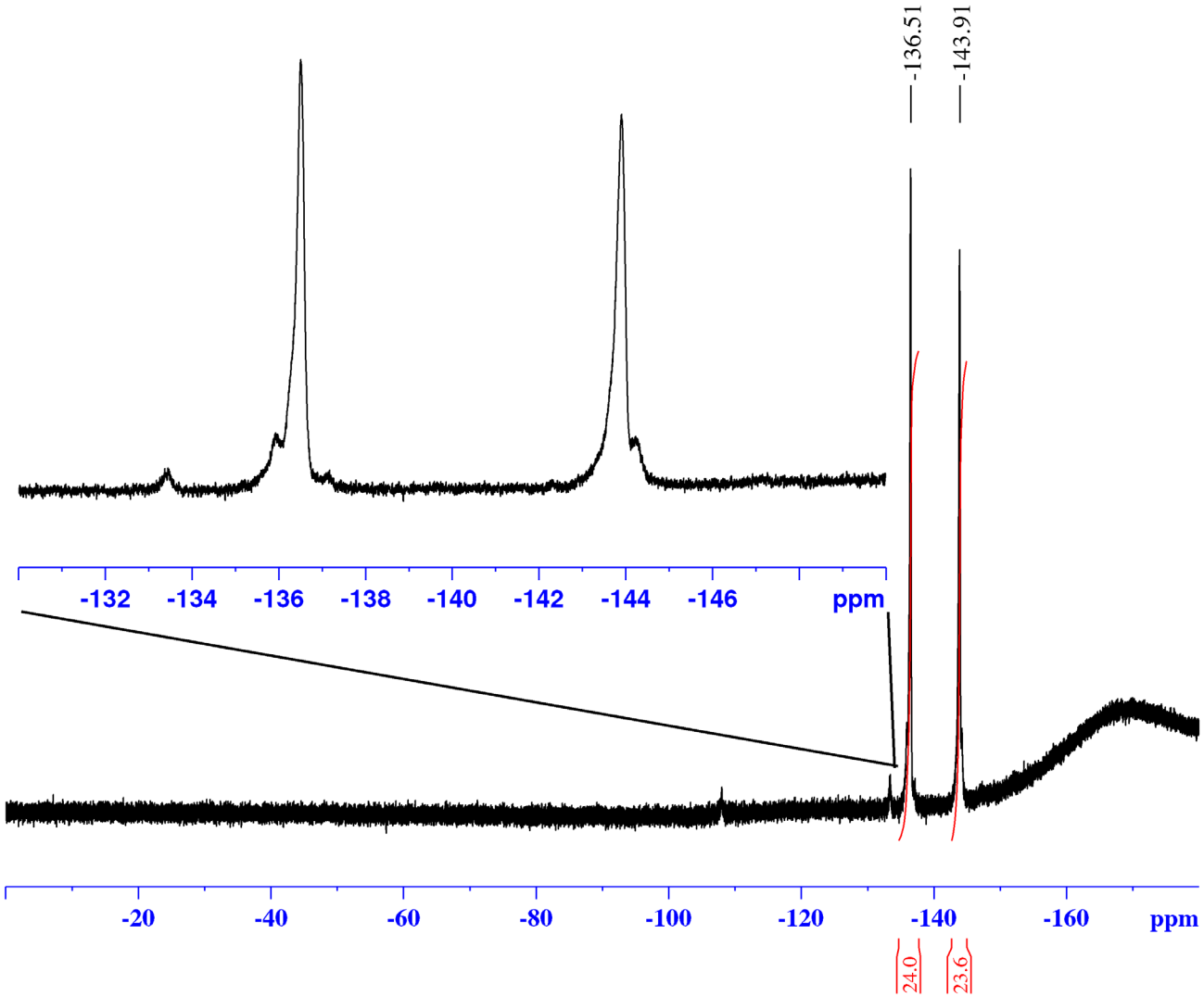
Current Data Parameters
NAME 0225
EXPNO 71
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160225
Time 16.57 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



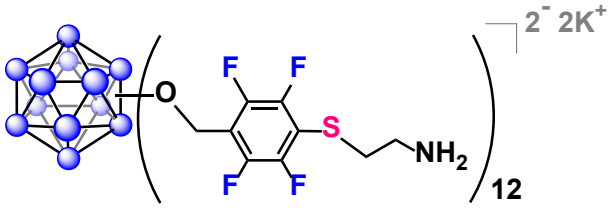
in situ ^{19}F NMR



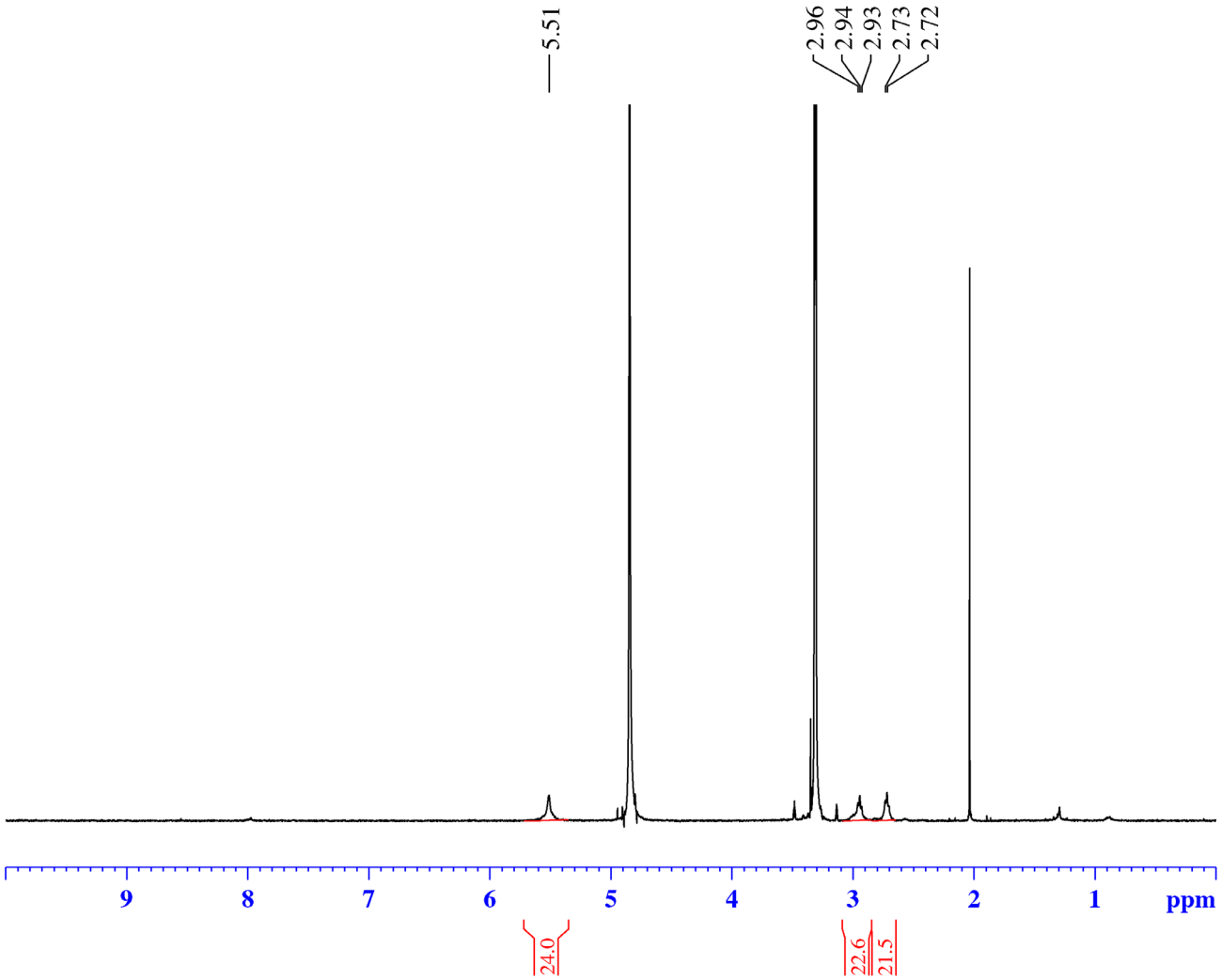
Current Data Parameters
NAME 0225
EXPNO 70
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160225
Time 16.54 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 1.144409 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



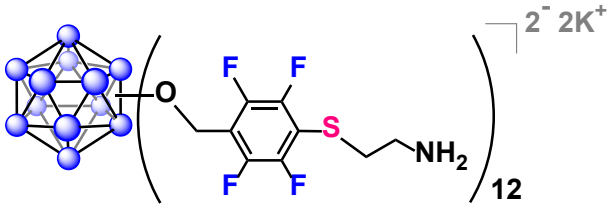
^{1}H NMR



Current Data Parameters
NAME G1 CA 0303 0224 (MeOD)
EXPNO 80
PROCNO 1

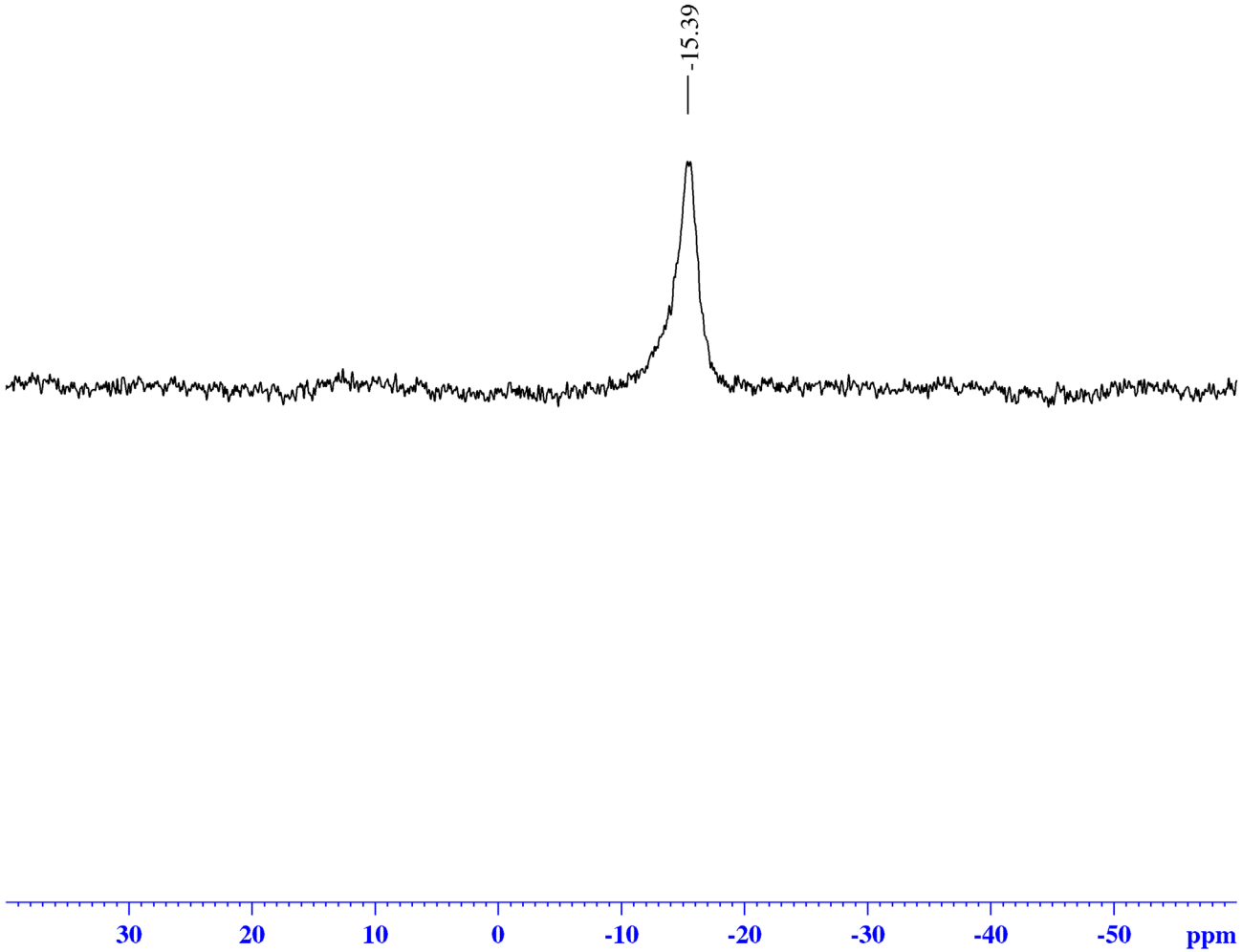
F2 - Acquisition Parameters
Date_ 20160303
Time 20.06 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.303045 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

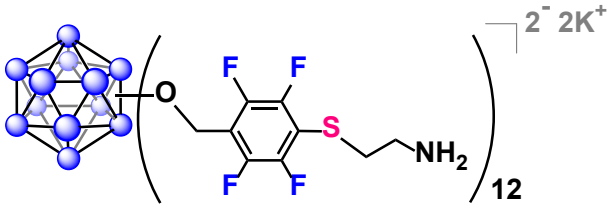
BRUKER



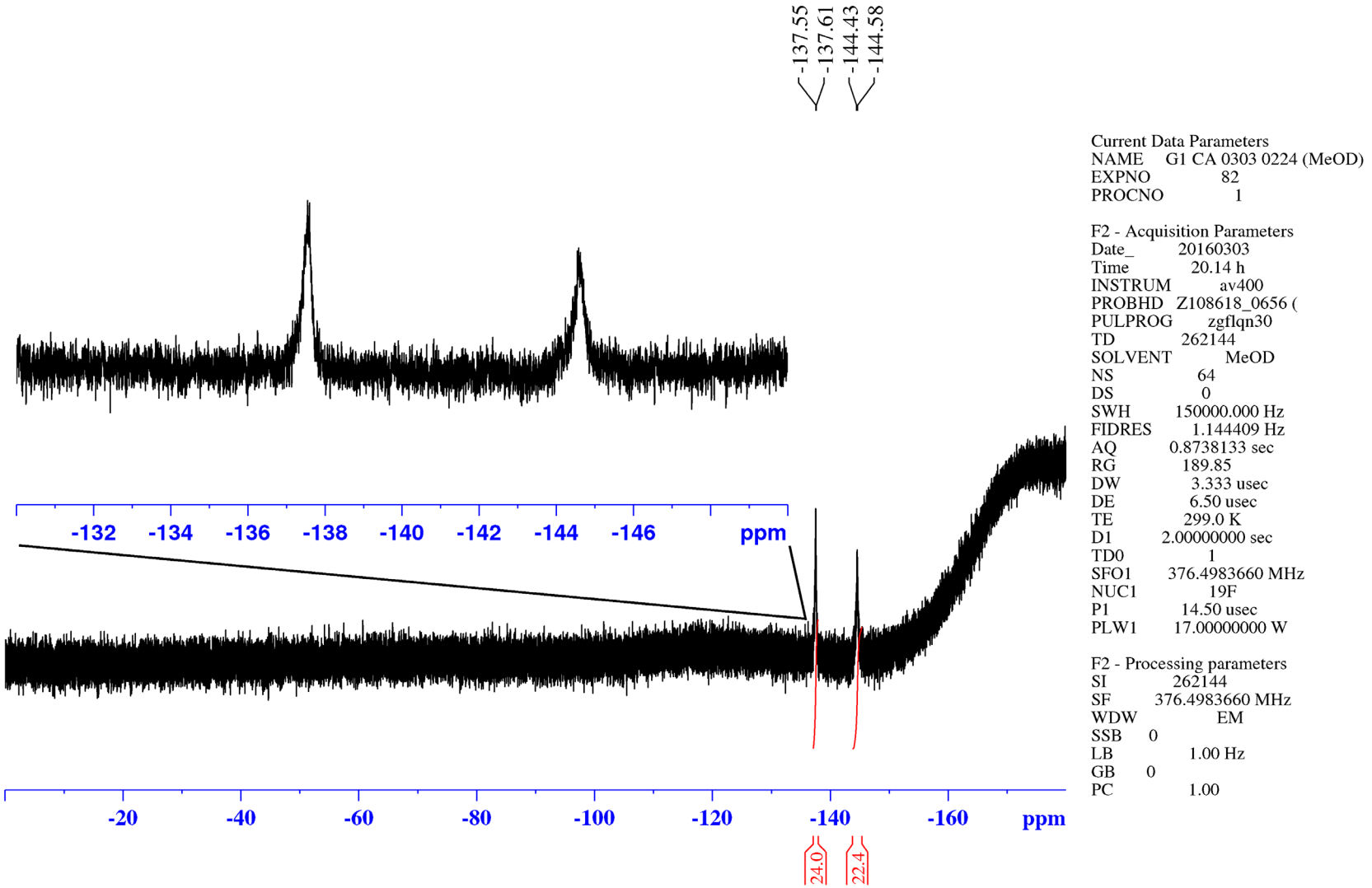
Current Data Parameters
NAME G1 CA 0303 0224 (MeOD)
EXPNO 81
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160303
Time 20.09 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



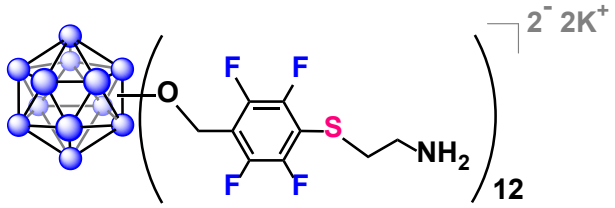
^{19}F NMR



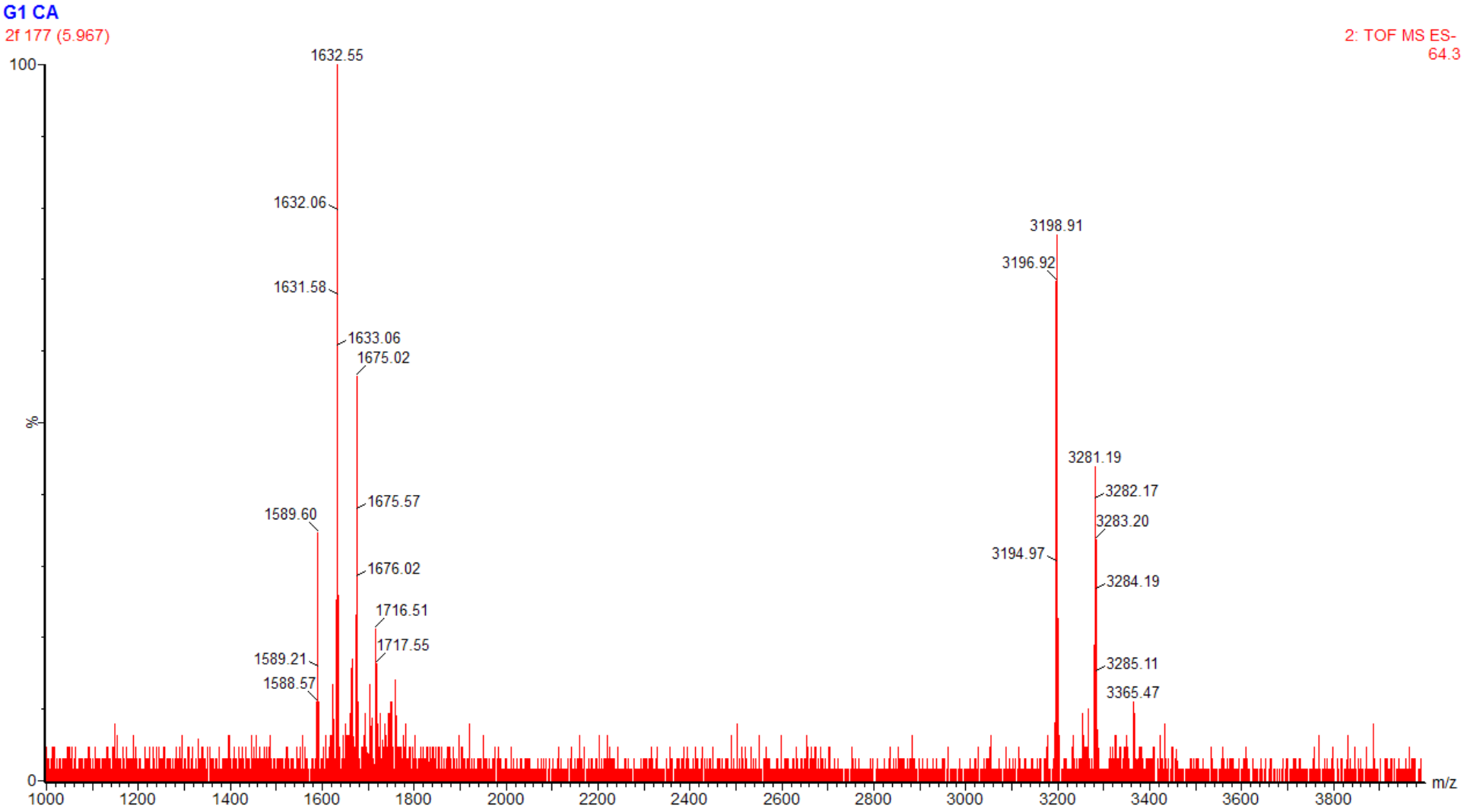
Current Data Parameters
NAME G1 CA 0303 0224 (MeOD)
EXPNO 82
PROCNO 1

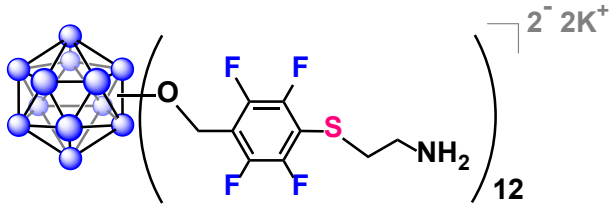
F2 - Acquisition Parameters
Date_ 20160303
Time 20.14 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 1.144409 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

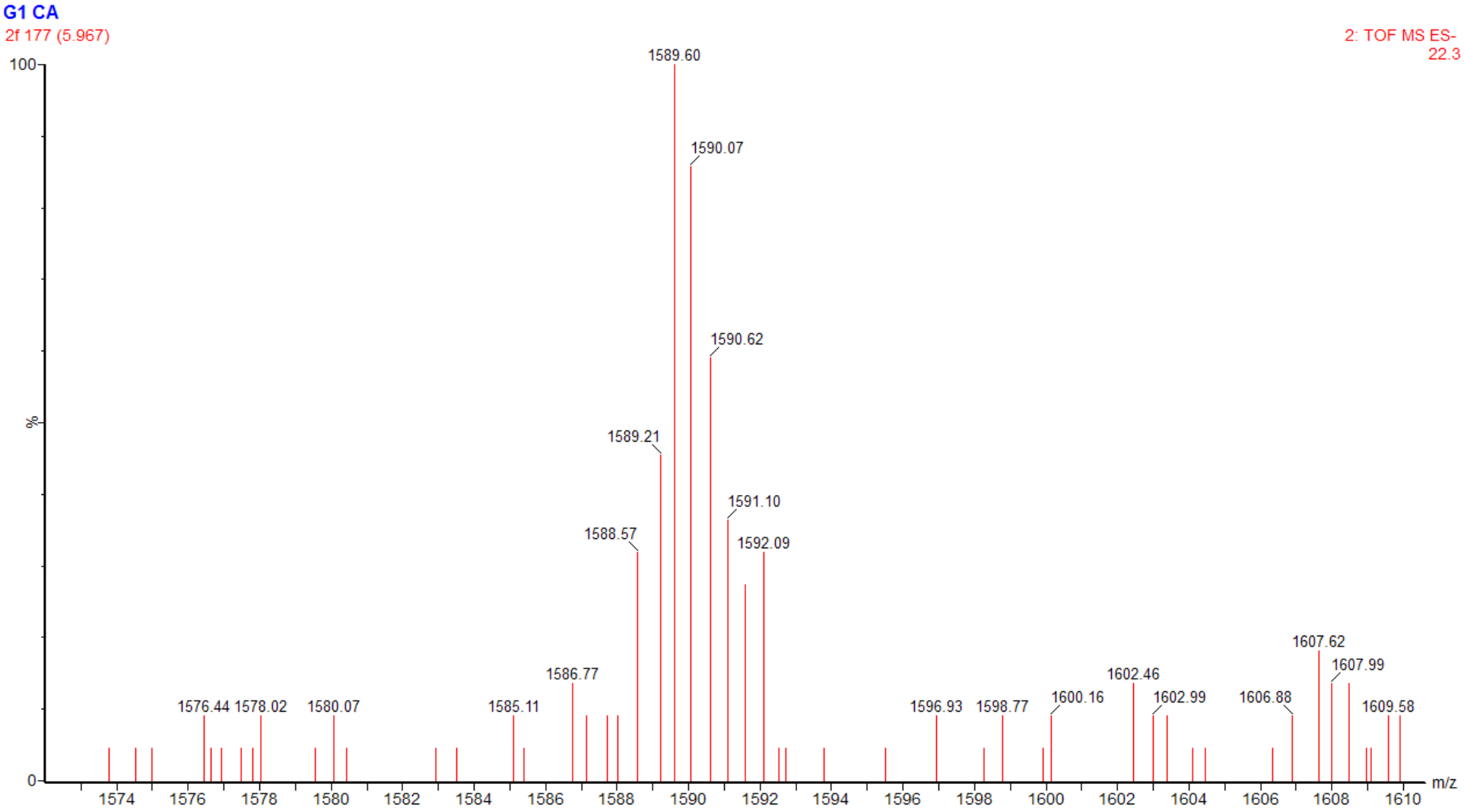


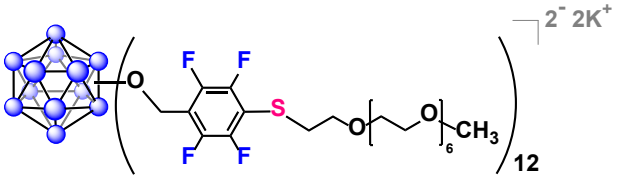
Waters
Mass Spec



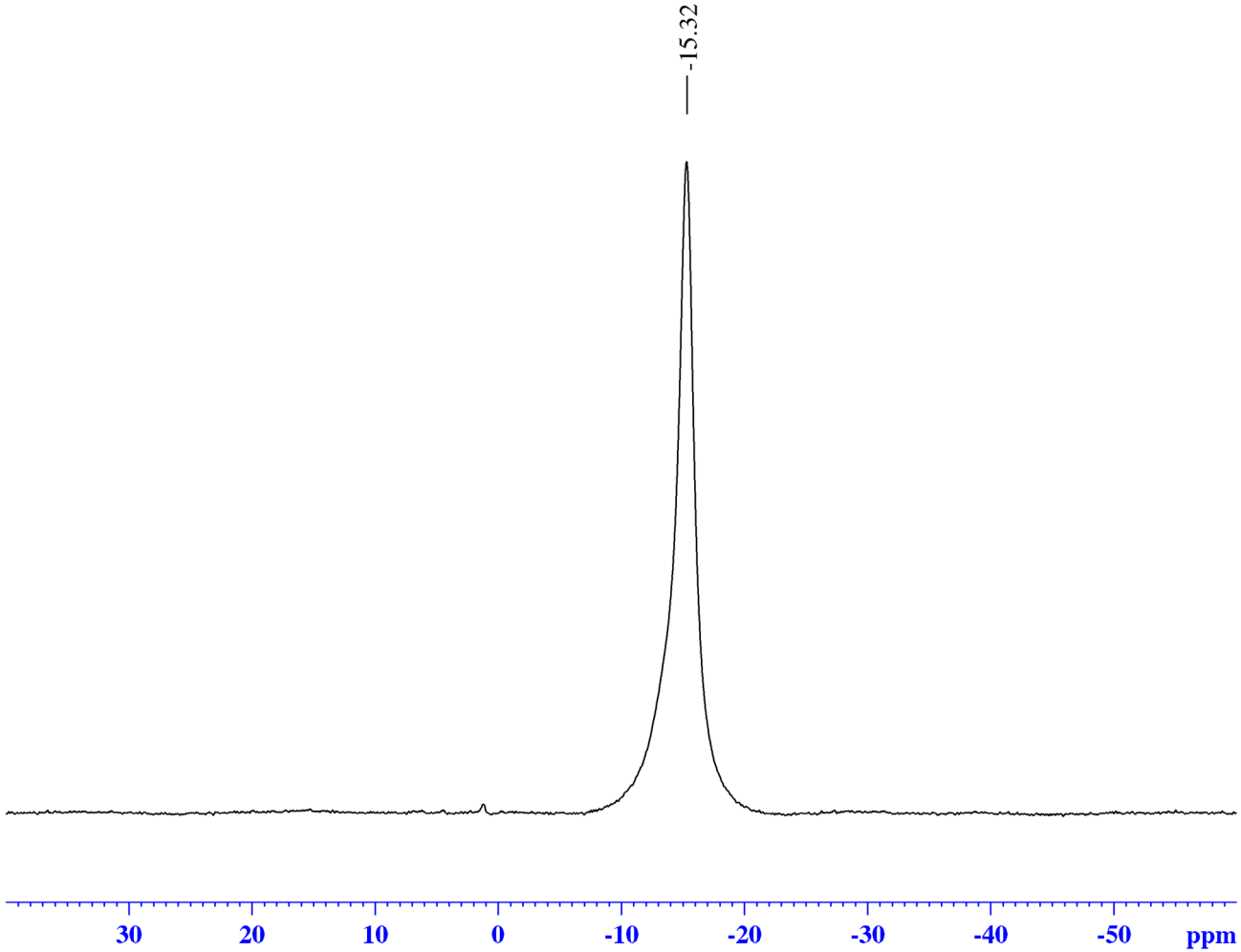


Waters
Mass Spec





in situ ^{11}B NMR

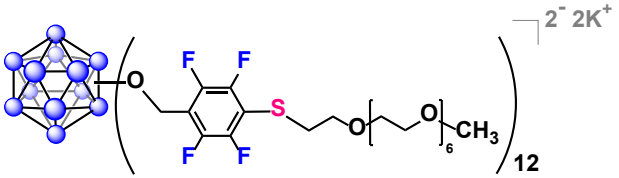


Current Data Parameters
NAME 0711
EXPNO 51
PROCNO 1

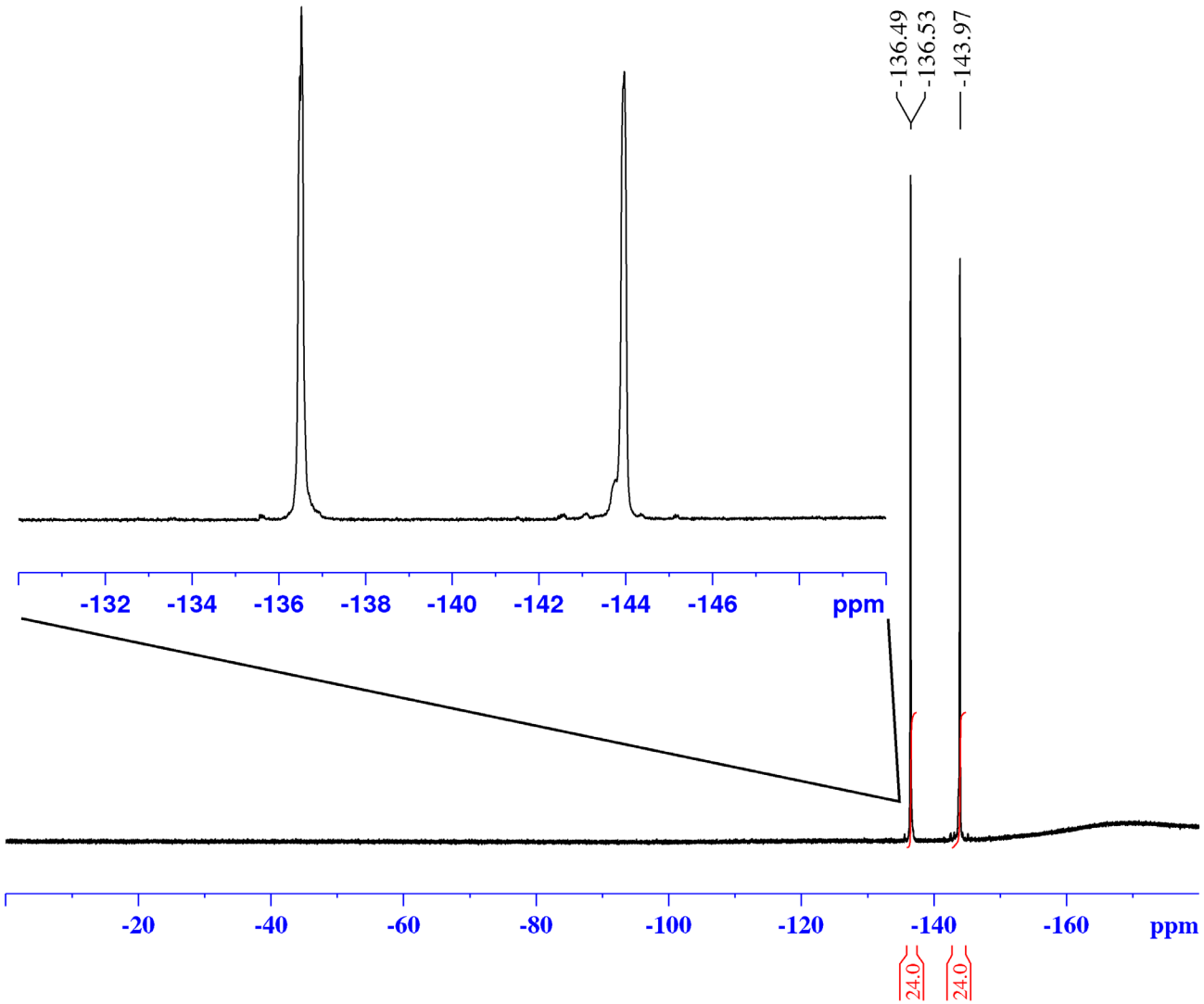
F2 - Acquisition Parameters
Date_ 20160711
Time 18.26
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

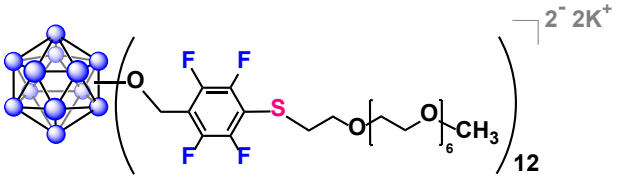


Current Data Parameters
NAME 0711
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160711
Time 18.23
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

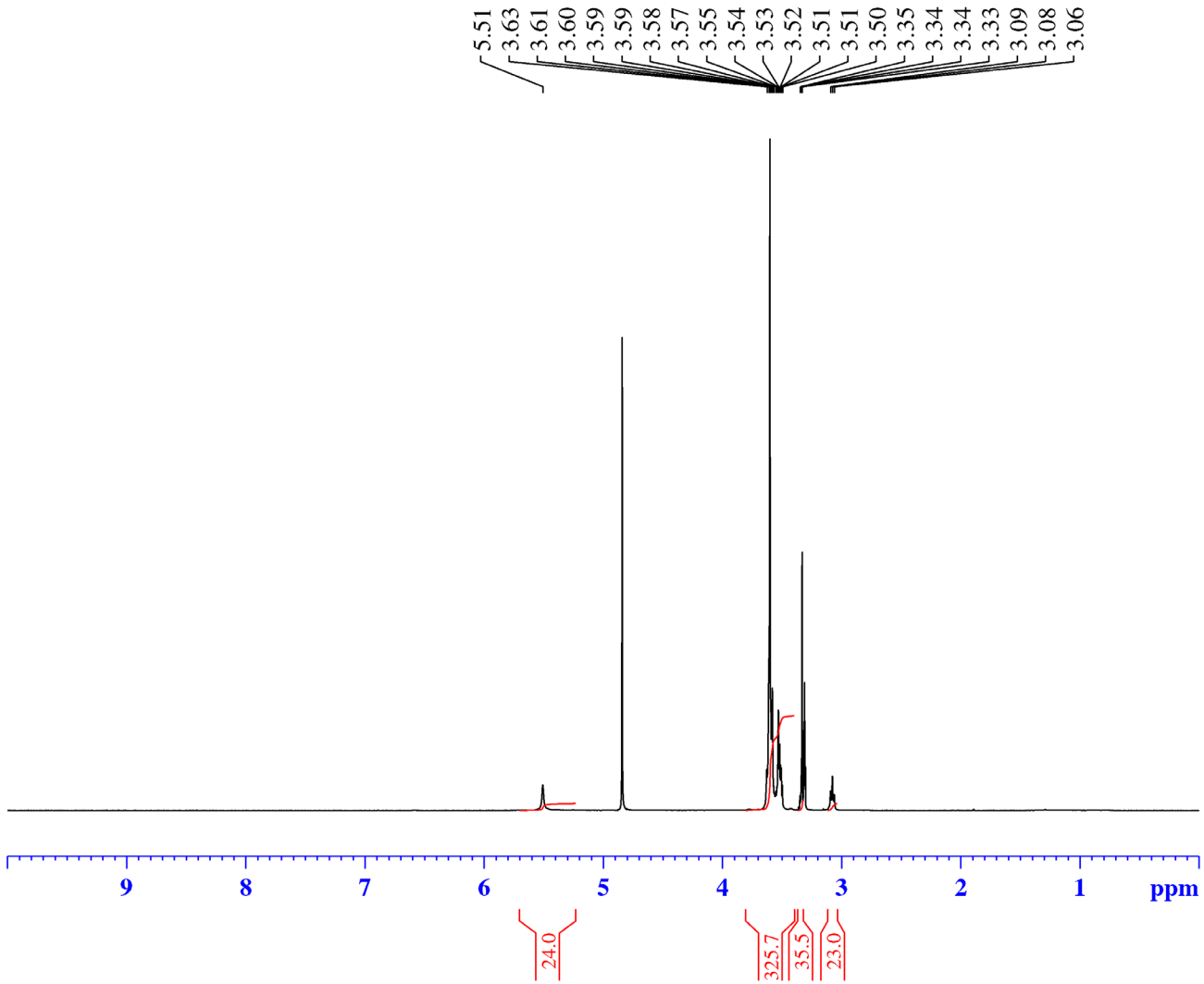
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

BRUKER

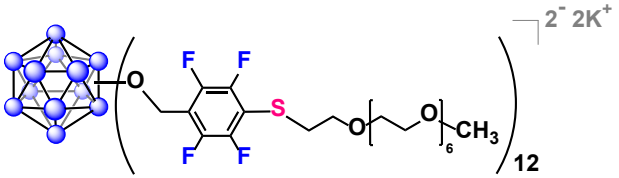


Current Data Parameters
NAME G1 PEG350 8 mg 0713 0710 (MeOD)
EXPNO 32
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160713
Time 15.01
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

BRUKER

-15.74

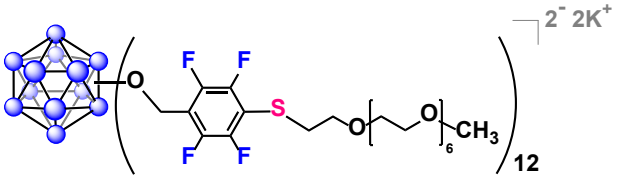
30 20 10 0 -10 -20 -30 -40 -50 ppm

Current Data Parameters
NAME G1 PEG350 8 mg 0713 0710 (MeOD)
EXPNO 30
PROCNO 1

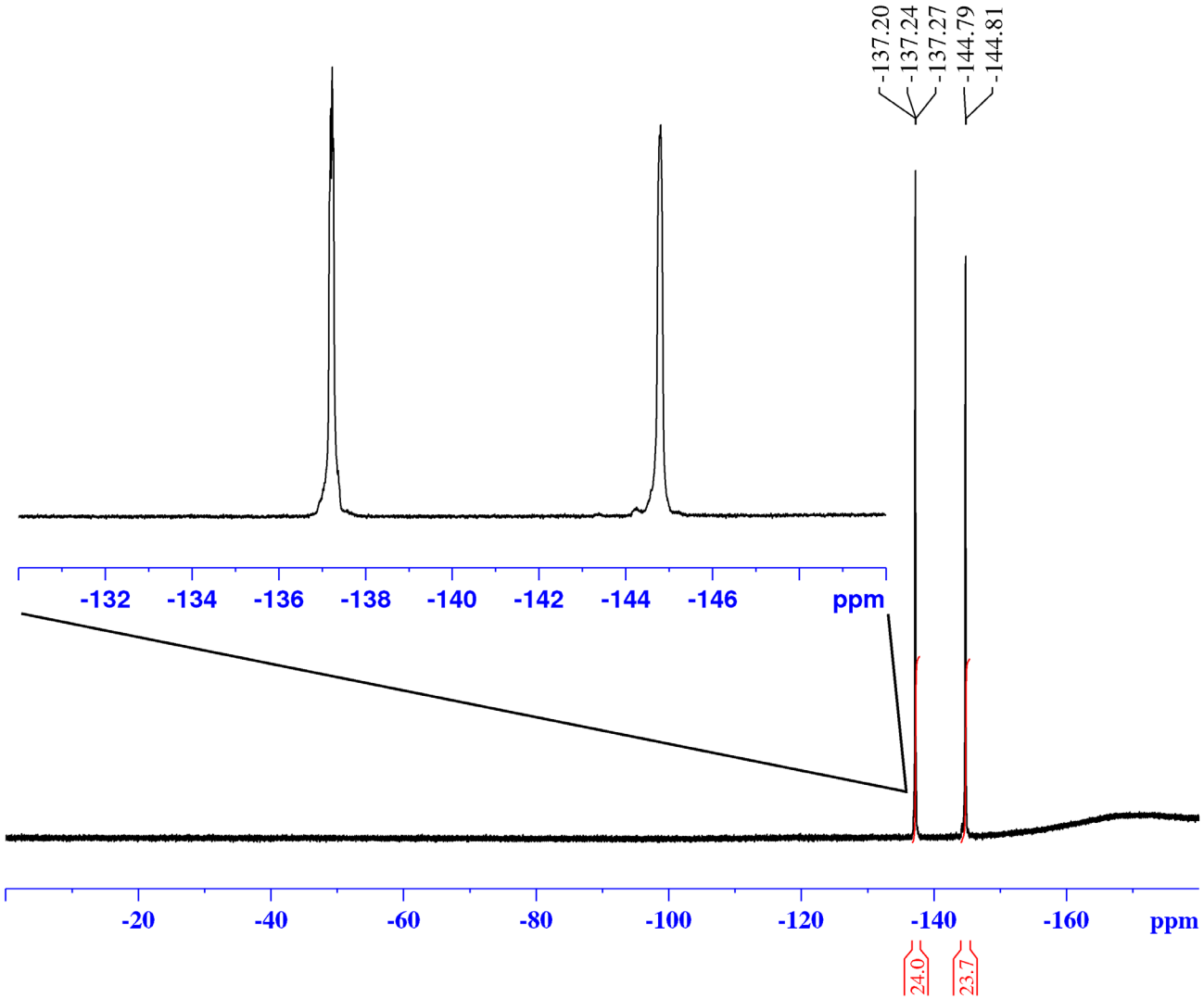
F2 - Acquisition Parameters
Date_ 20160713
Time 14.52
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

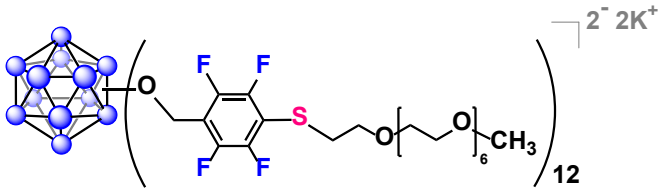


Current Data Parameters
NAME G1 PEG350 8 mg 0713 0710 (MeOD)
EXPNO 31
PROCNO 1

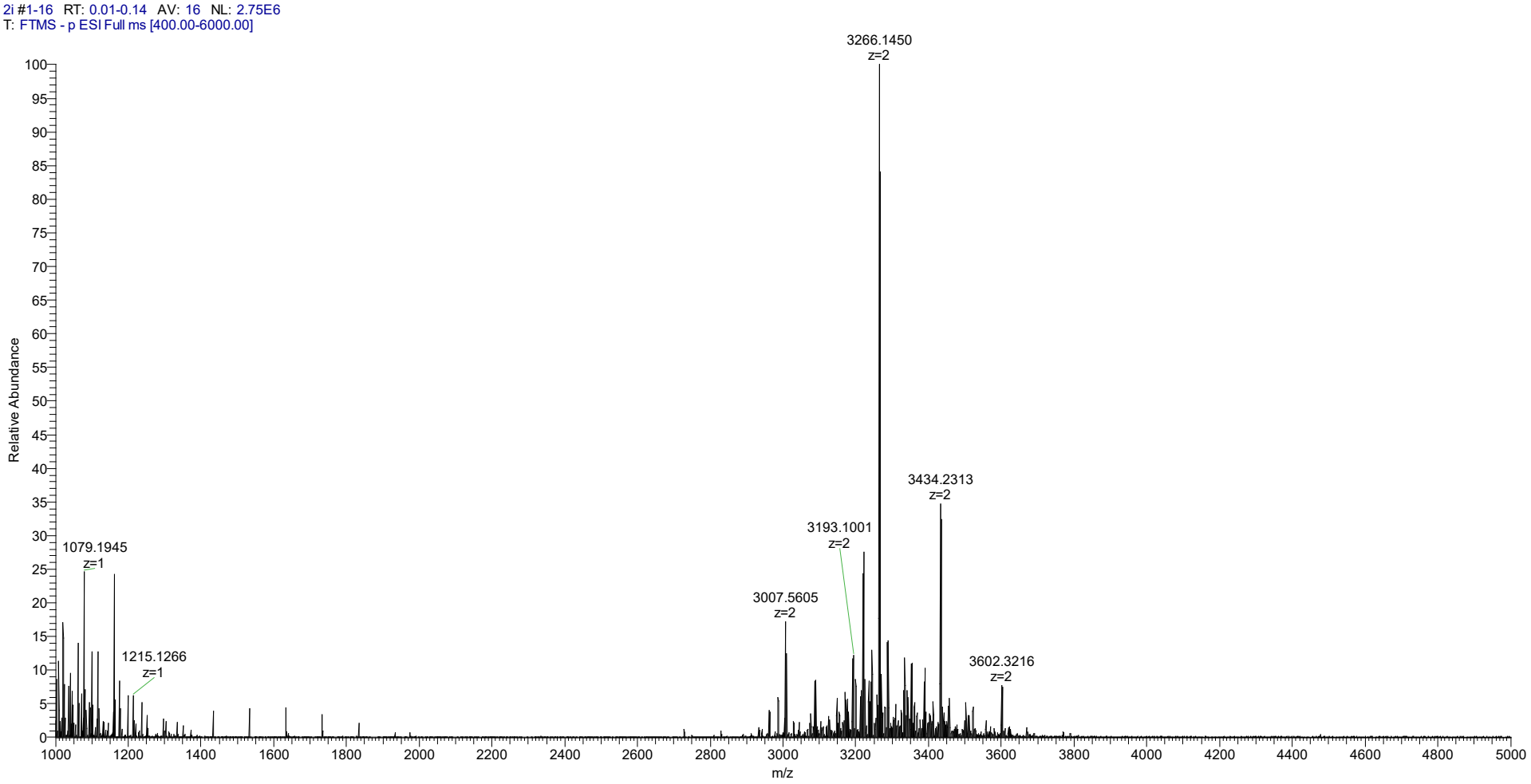
F2 - Acquisition Parameters
Date_ 20160713
Time 14.56
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

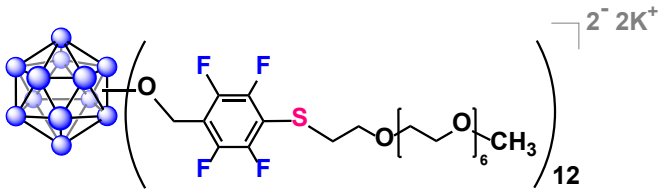
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



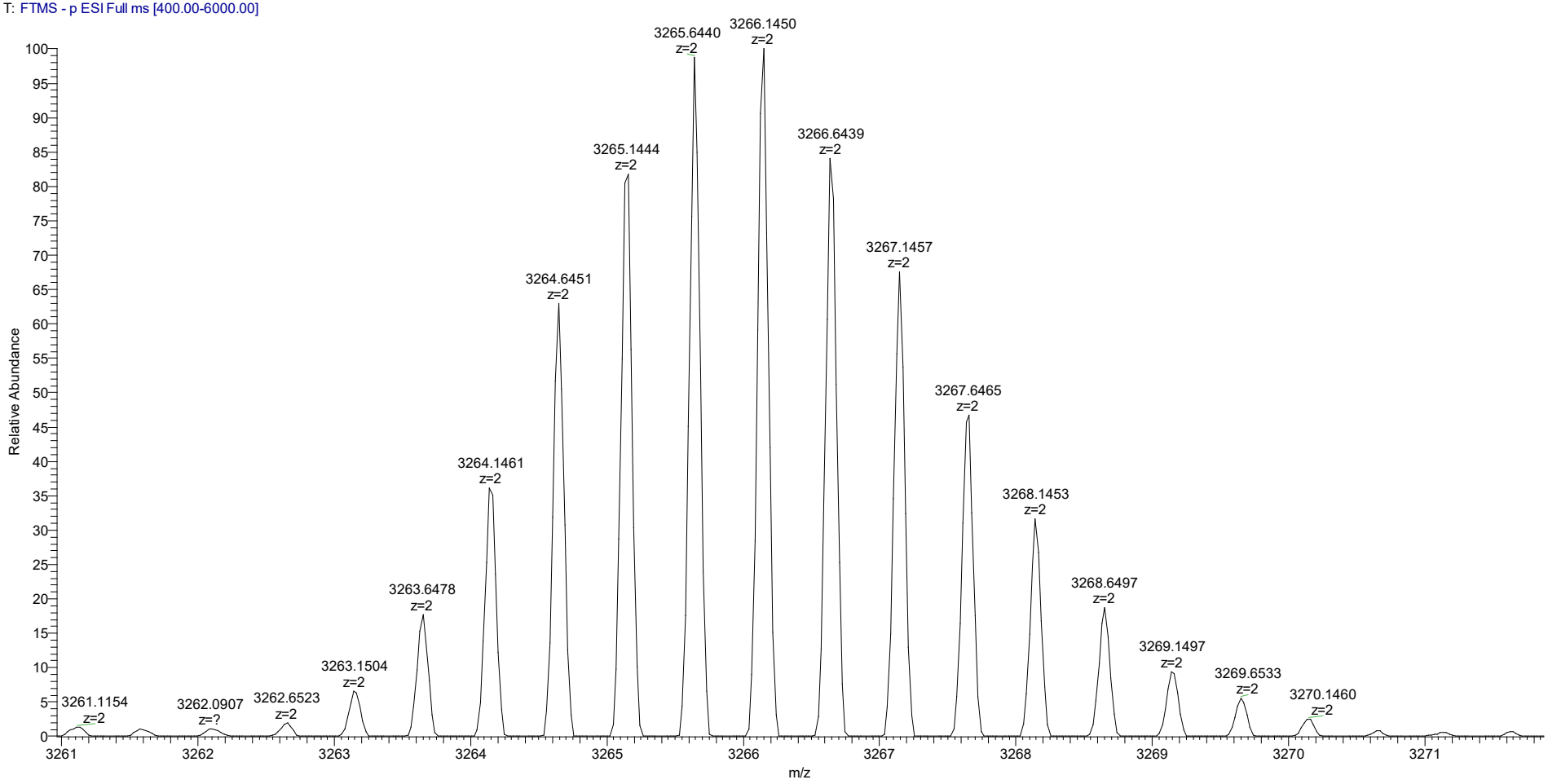
Q Exactive
High-Res Mass Spec

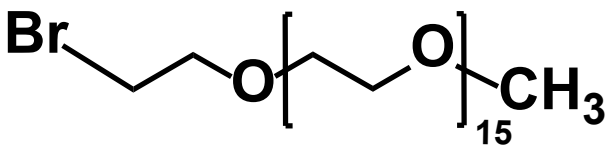




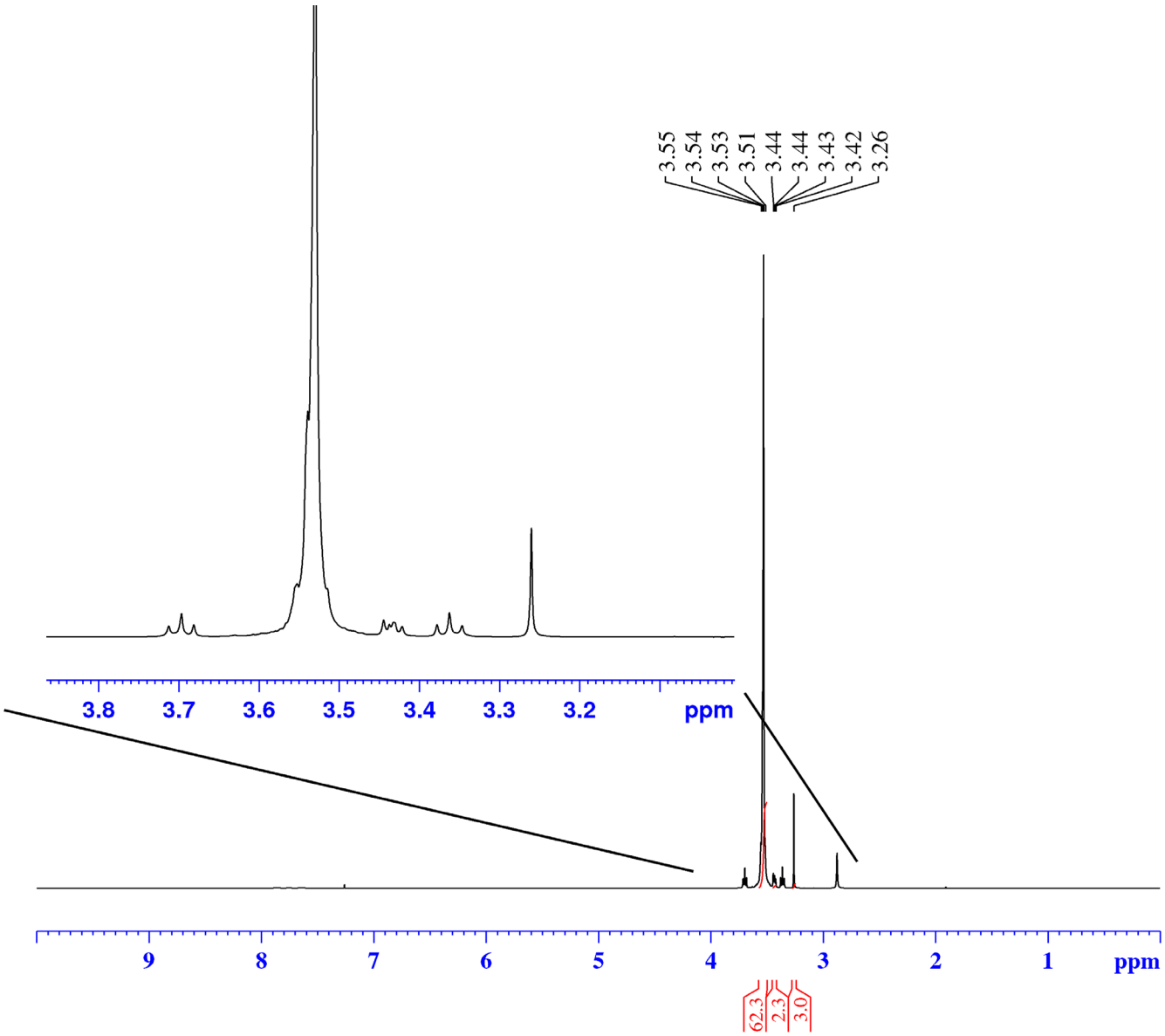
Q Exactive
High-Res Mass Spec

2i #1-16 RT: 0.01-0.14 AV: 16 NL: 2.75E6
T: FTMS - p ESI Full ms [400.00-6000.00]





^{1}H NMR

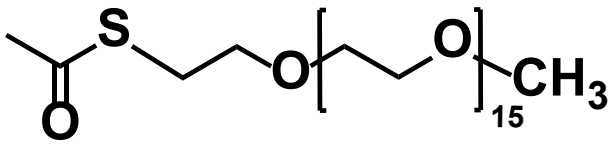


Current Data Parameters
NAME mPEG-Br
EXPNO 60
PROCNO 1

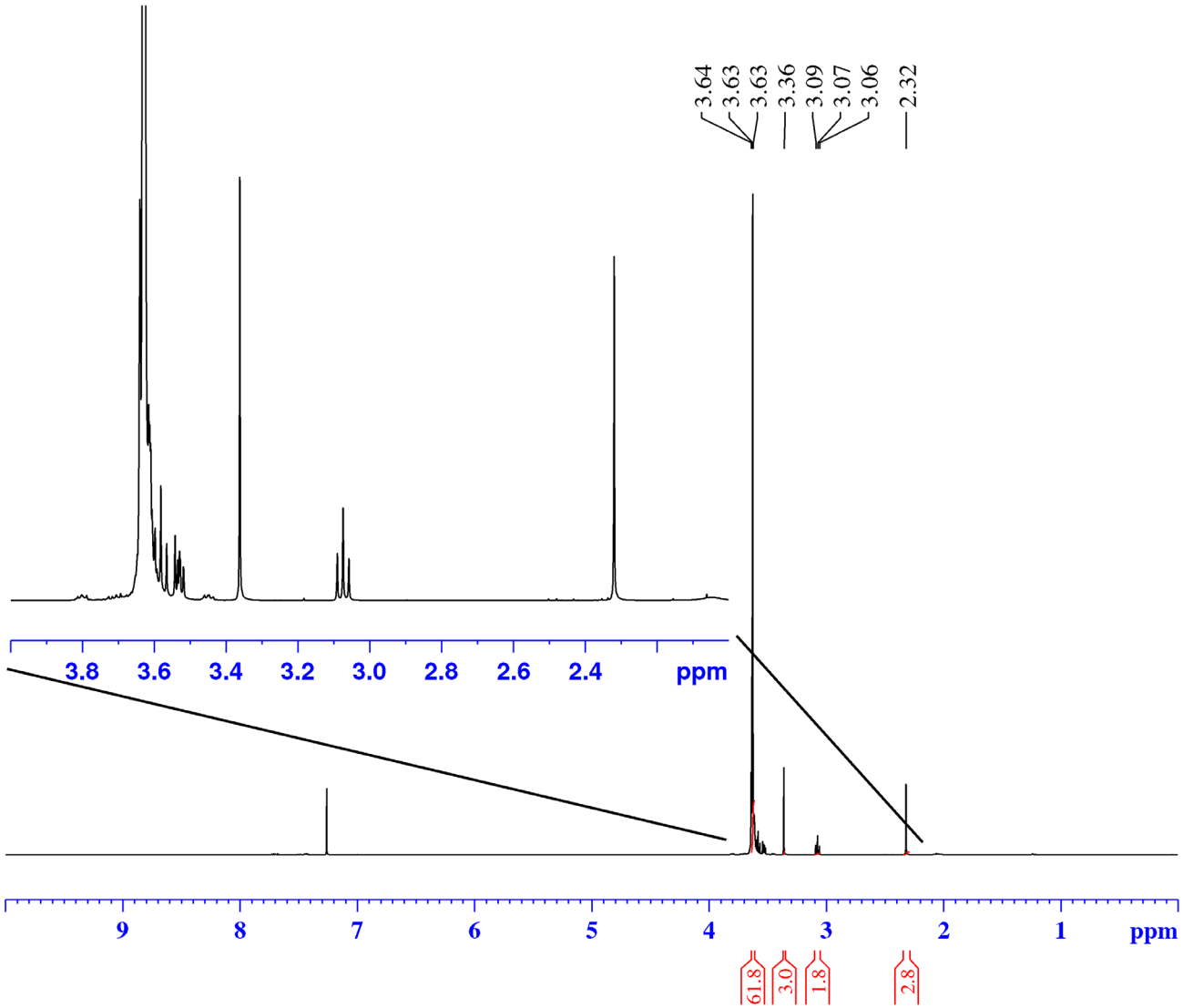
F2 - Acquisition Parameters
Date_ 20151213
Time 15.05
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 64
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 12.23
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{1}H NMR

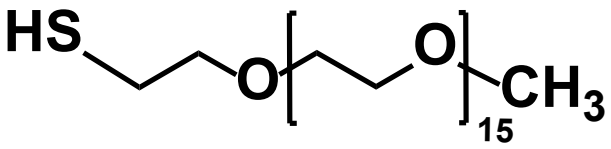


Current Data Parameters
NAME mPEG-SAc
EXPNO 160
PROCNO 1

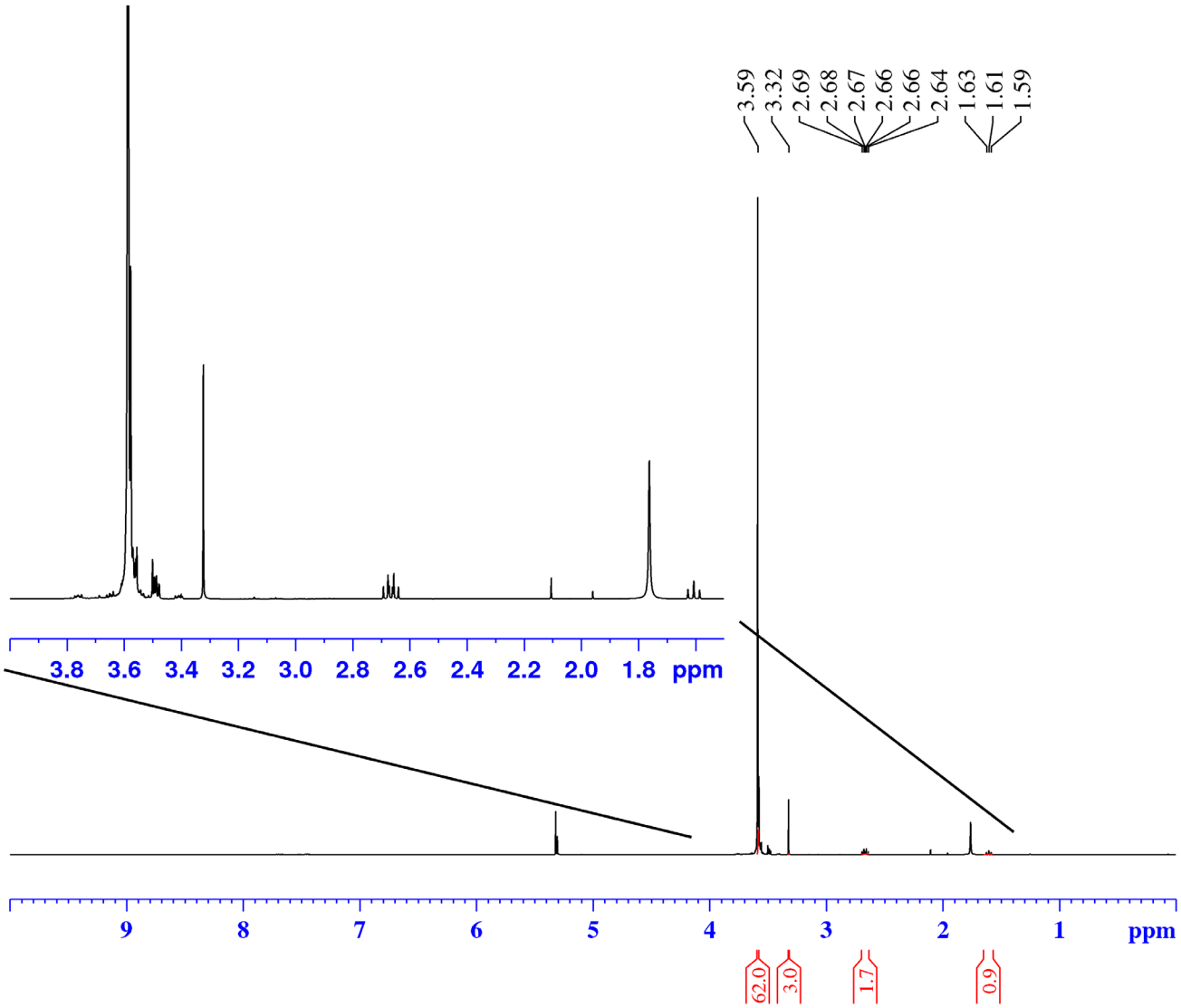
F2 - Acquisition Parameters
Date_ 20151215
Time 17.02
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 80
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 73.86
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{1}H NMR

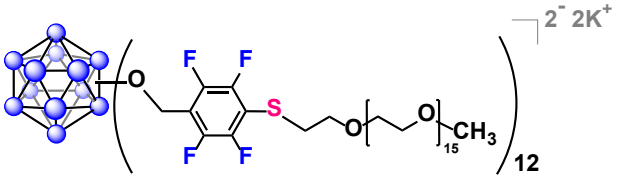


Current Data Parameters
NAME mPEG-SH
EXPNO 80
PROCNO 1

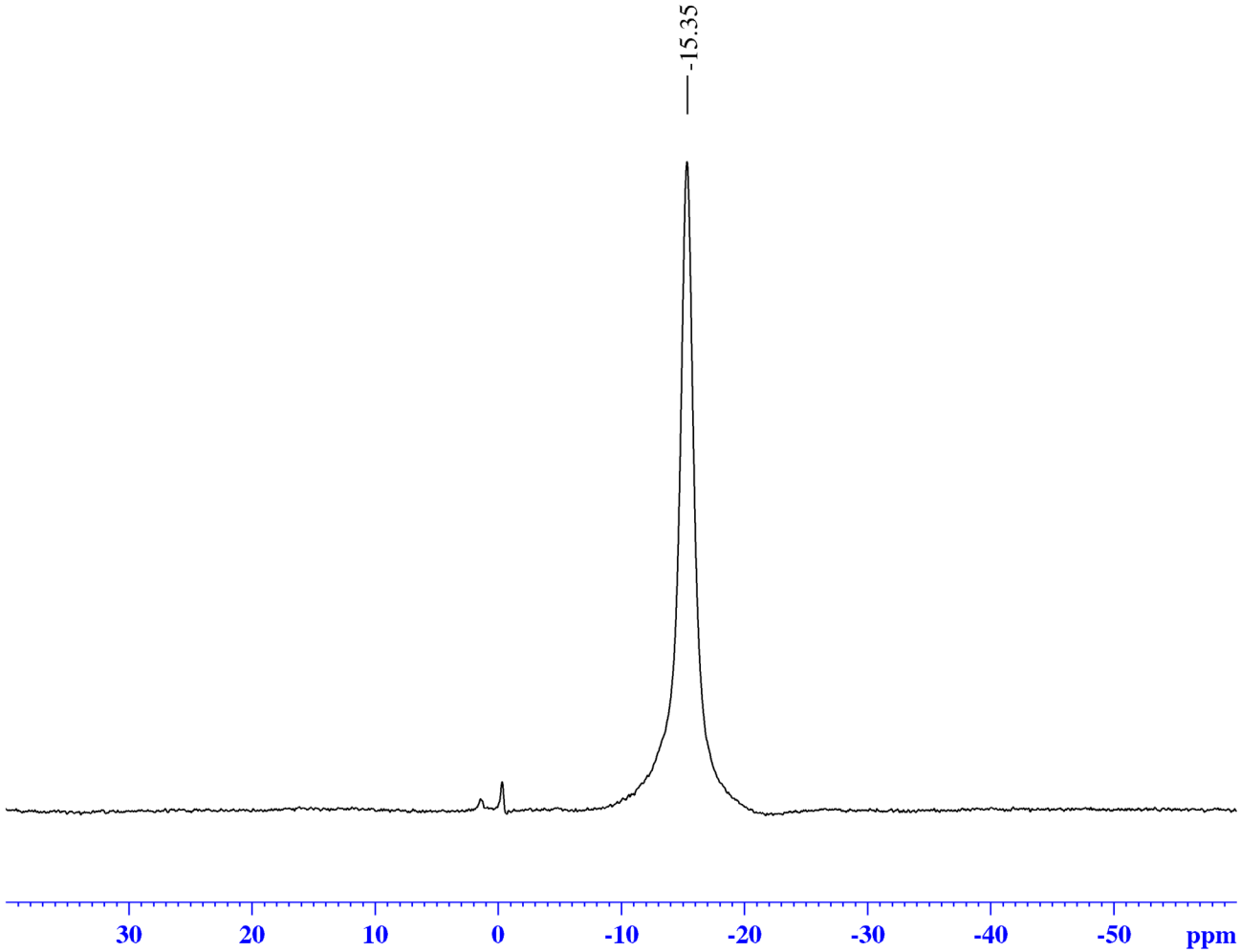
F2 - Acquisition Parameters
Date_ 20151216
Time 19.25
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CD2Cl2
NS 80
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300203 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



in situ ^{11}B NMR

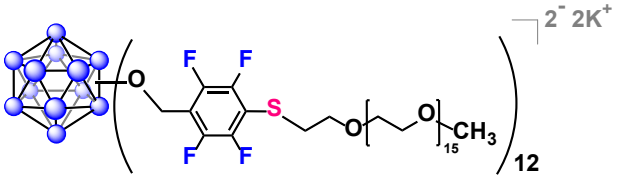


Current Data Parameters
NAME 0209
EXPNO 91
PROCNO 1

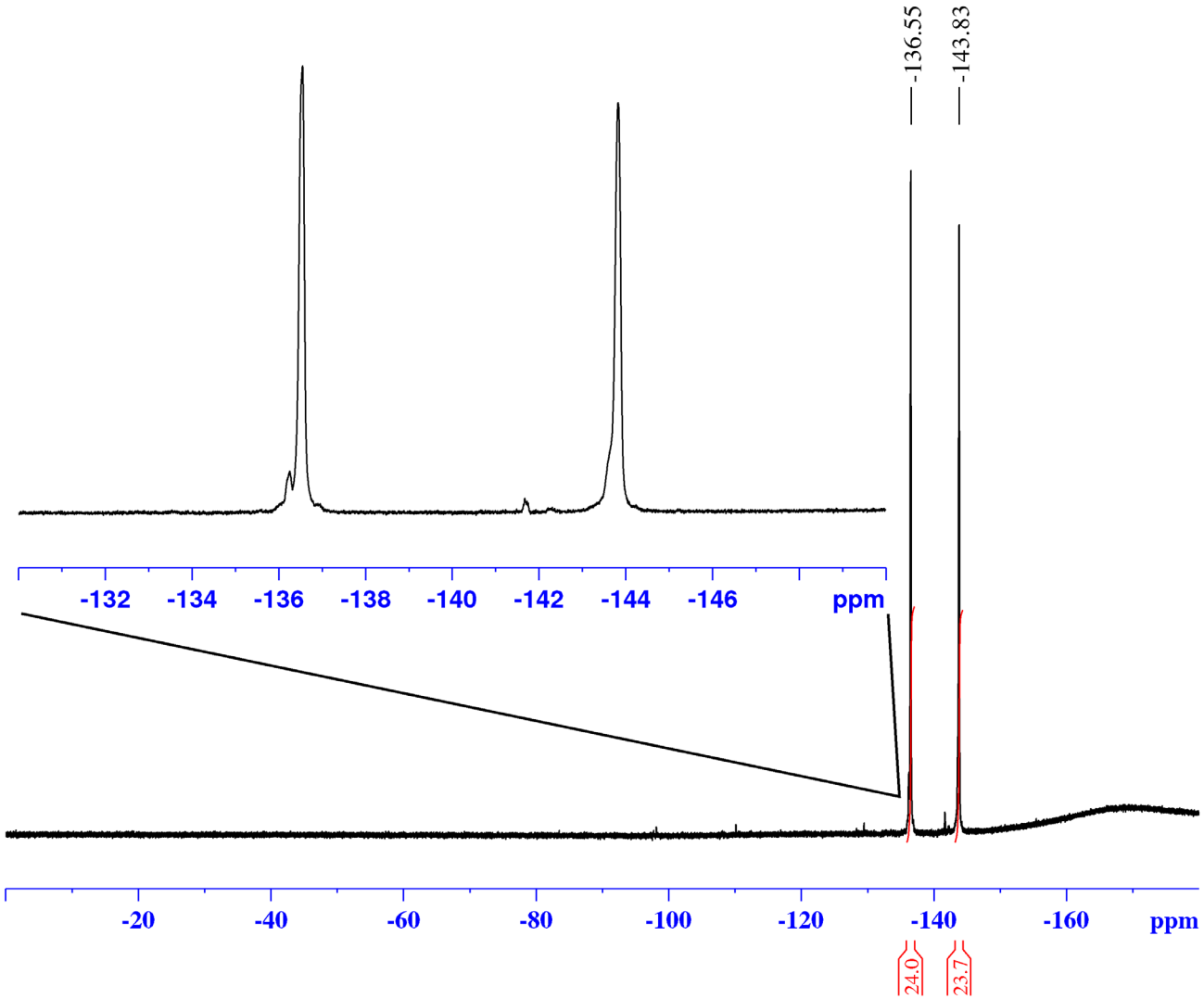
F2 - Acquisition Parameters
Date_ 20160209
Time 19.27
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

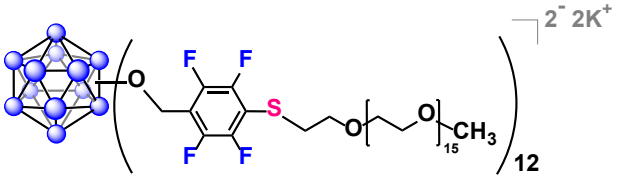


Current Data Parameters
NAME 0209
EXPNO 90
PROCNO 1

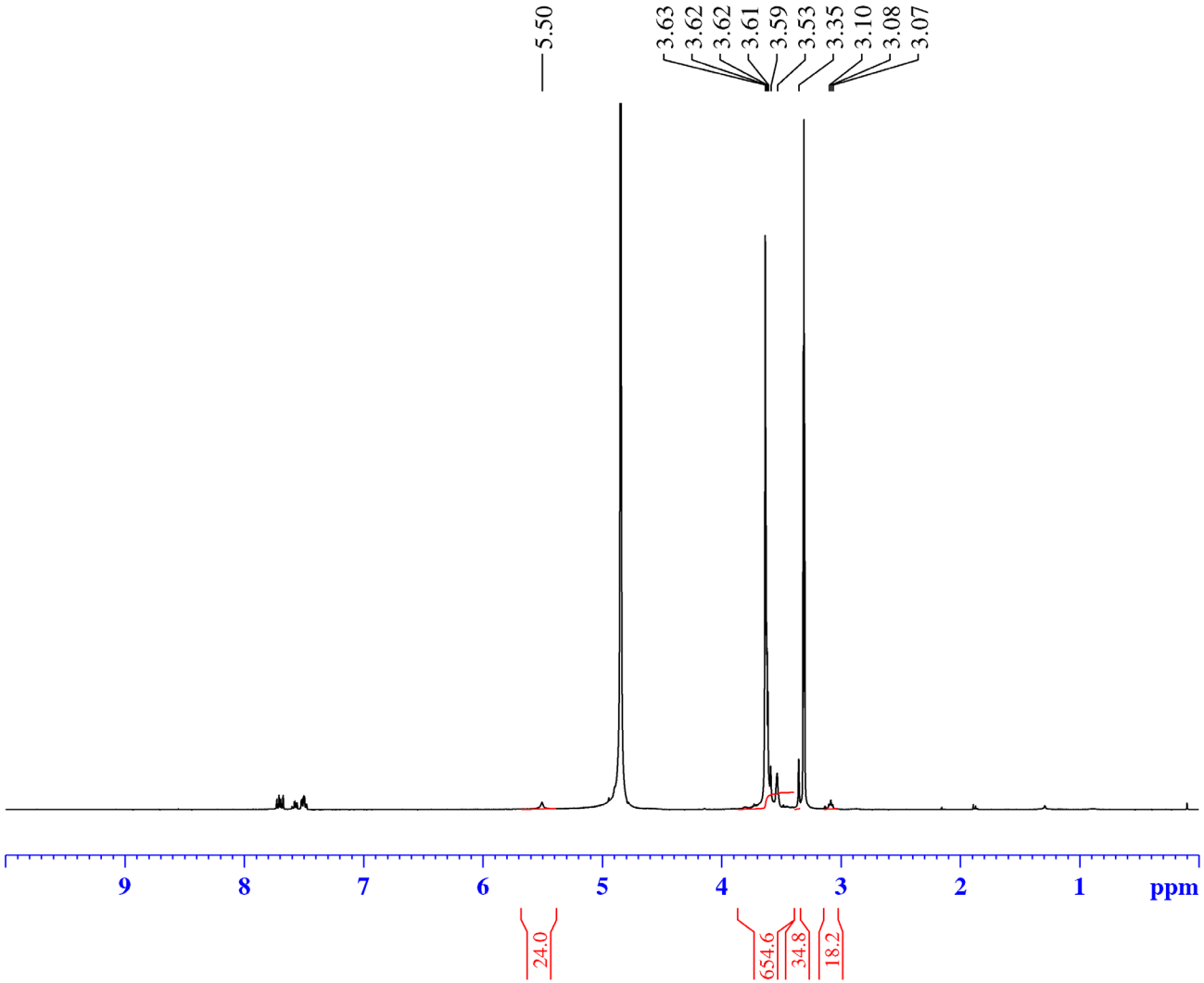
F2 - Acquisition Parameters
Date_ 20160209
Time 19.24
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

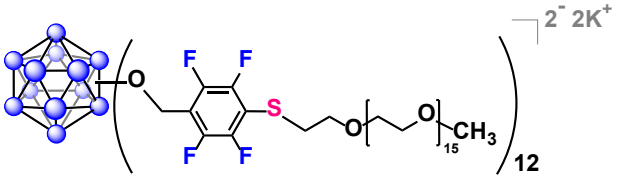


Current Data Parameters
NAME G1 PEG750 0211 0208 MeOD
EXPNO 170
PROCNO 1

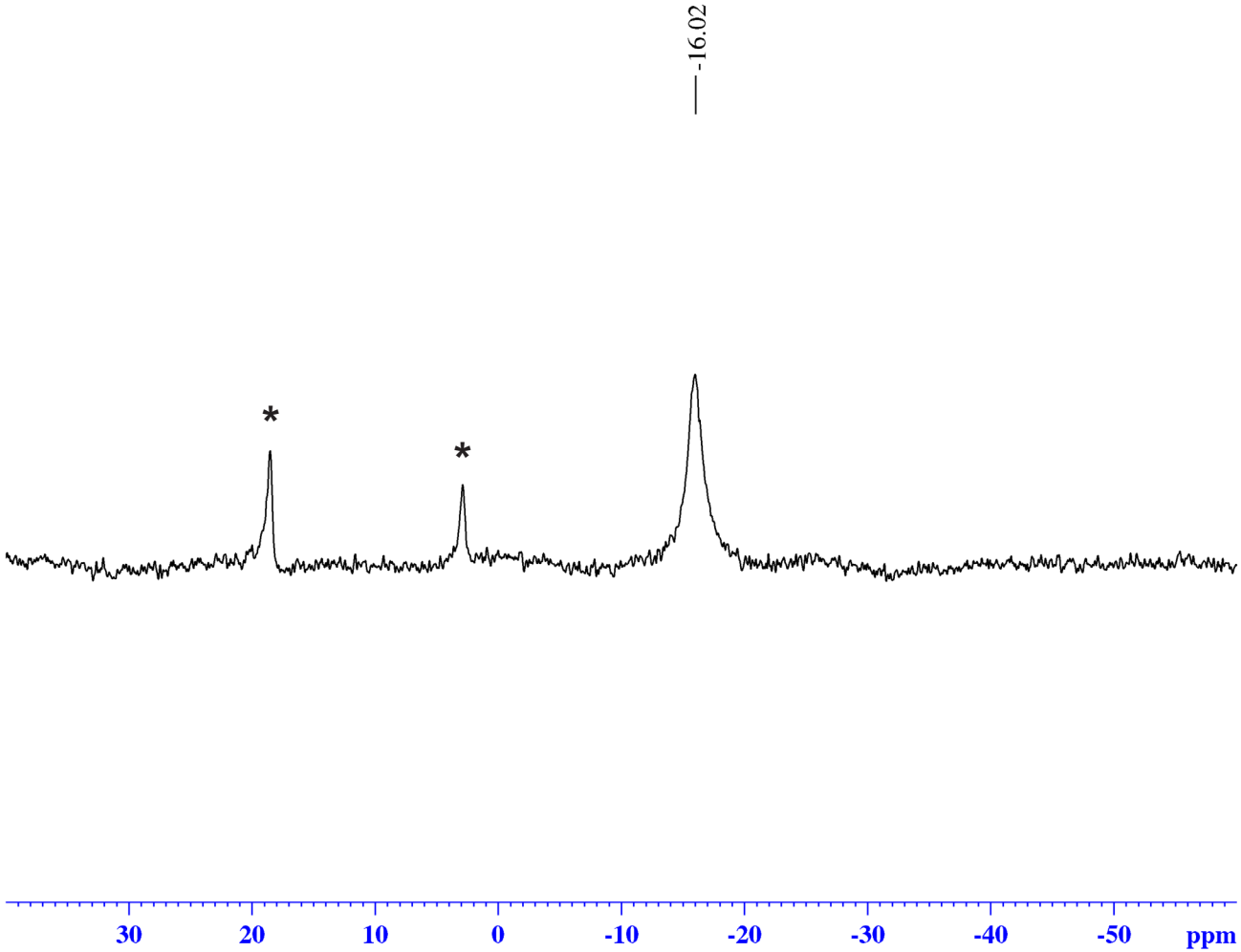
F2 - Acquisition Parameters
Date_ 20160213
Time 20.35
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300079 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR



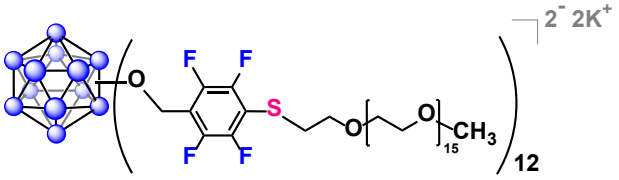
Current Data Parameters
NAME G1 PEG750 0211 0208 MeOD
EXPNO 171
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160213
Time 20.38
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

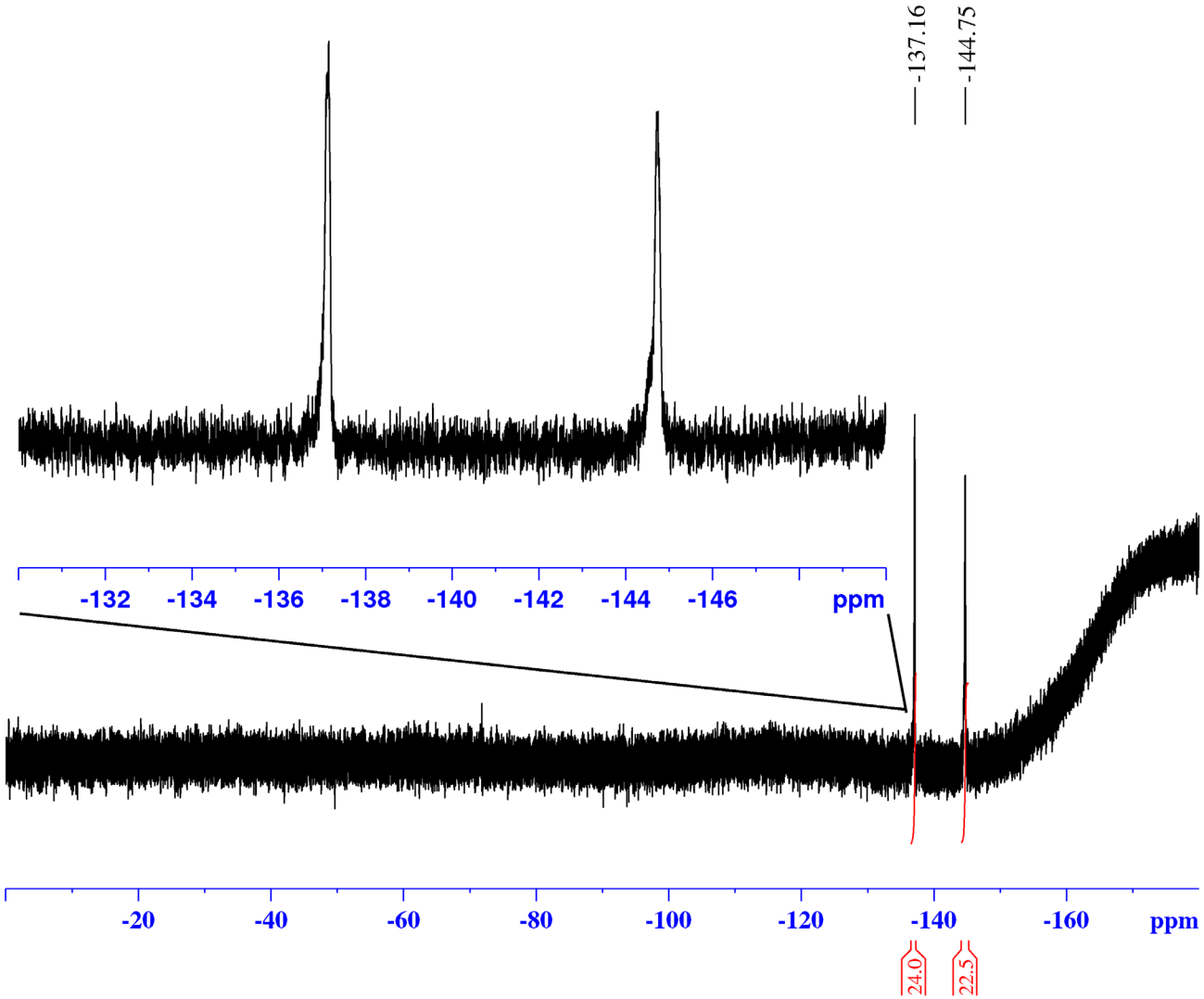
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

* These peaks correspond to small impurities - boric acid and borates.



^{19}F NMR

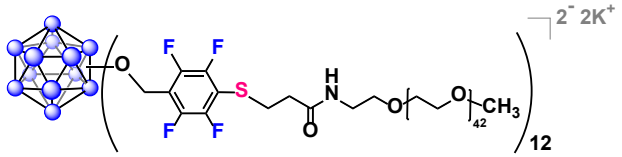


Current Data Parameters
NAME G1 PEG750 0211 0208 MeOD
EXPNO 172
PROCNO 1

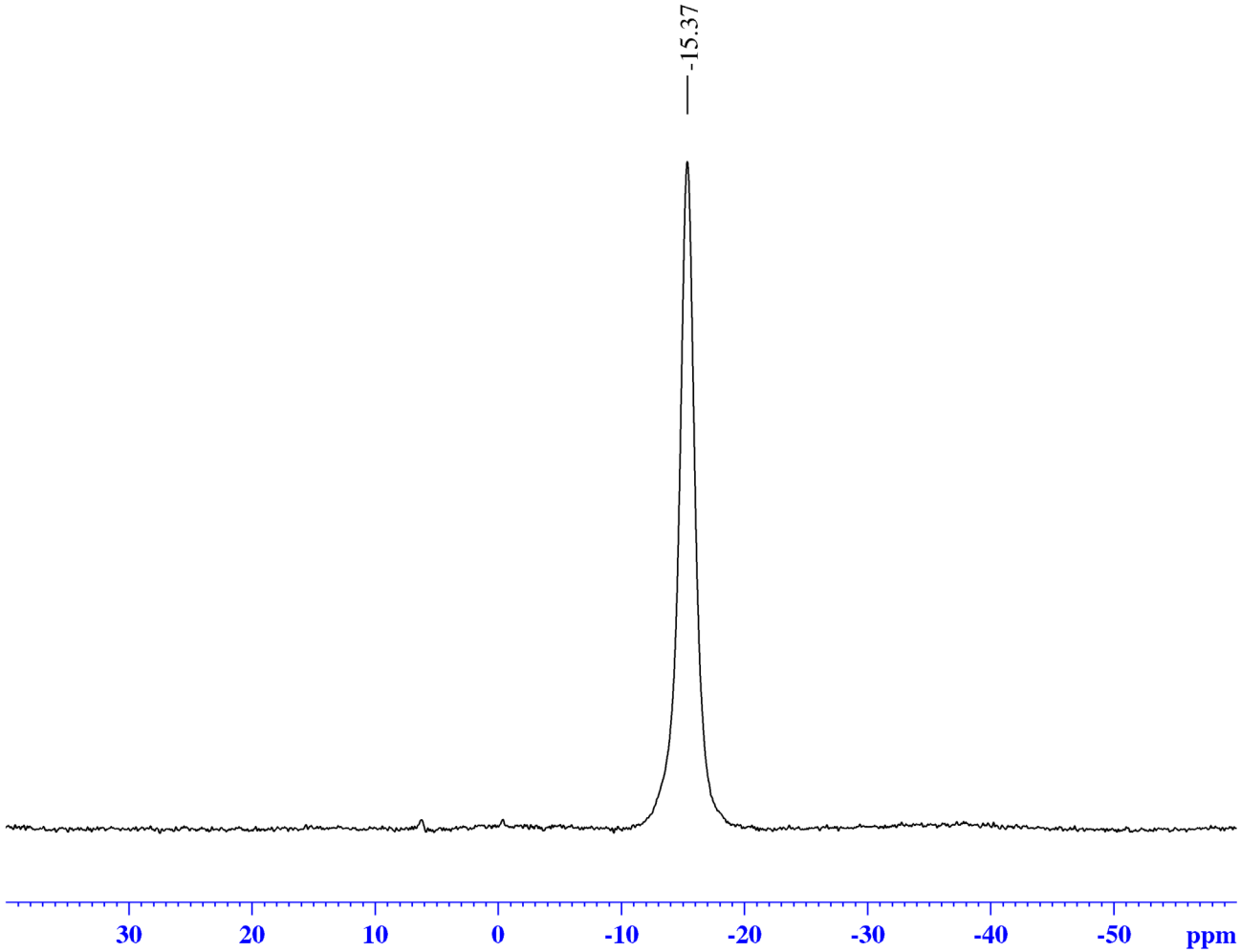
F2 - Acquisition Parameters
Date_ 20160213
Time 20.42
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



in situ ^{11}B NMR

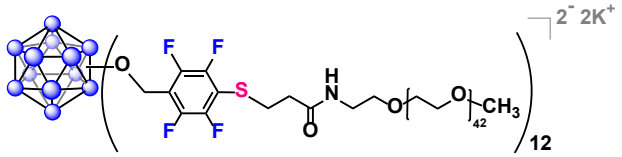


Current Data Parameters
NAME 0209
EXPNO 101
PROCNO 1

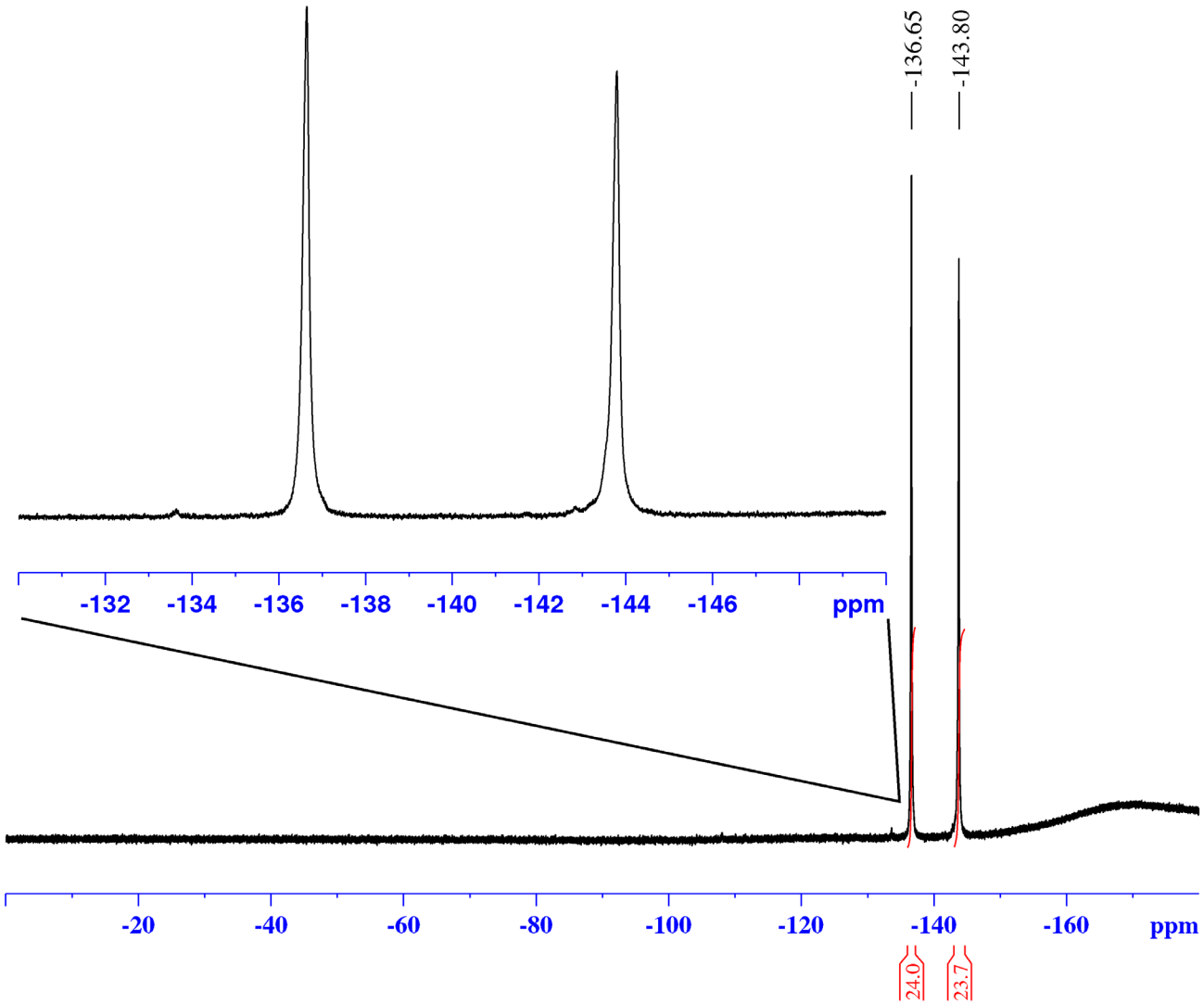
F2 - Acquisition Parameters
Date_ 20160209
Time 19.36
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

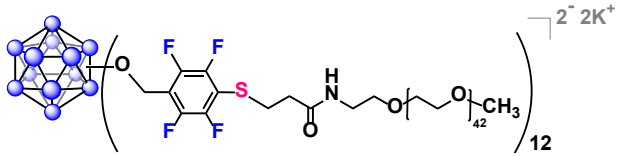


Current Data Parameters
NAME 0209
EXPNO 100
PROCNO 1

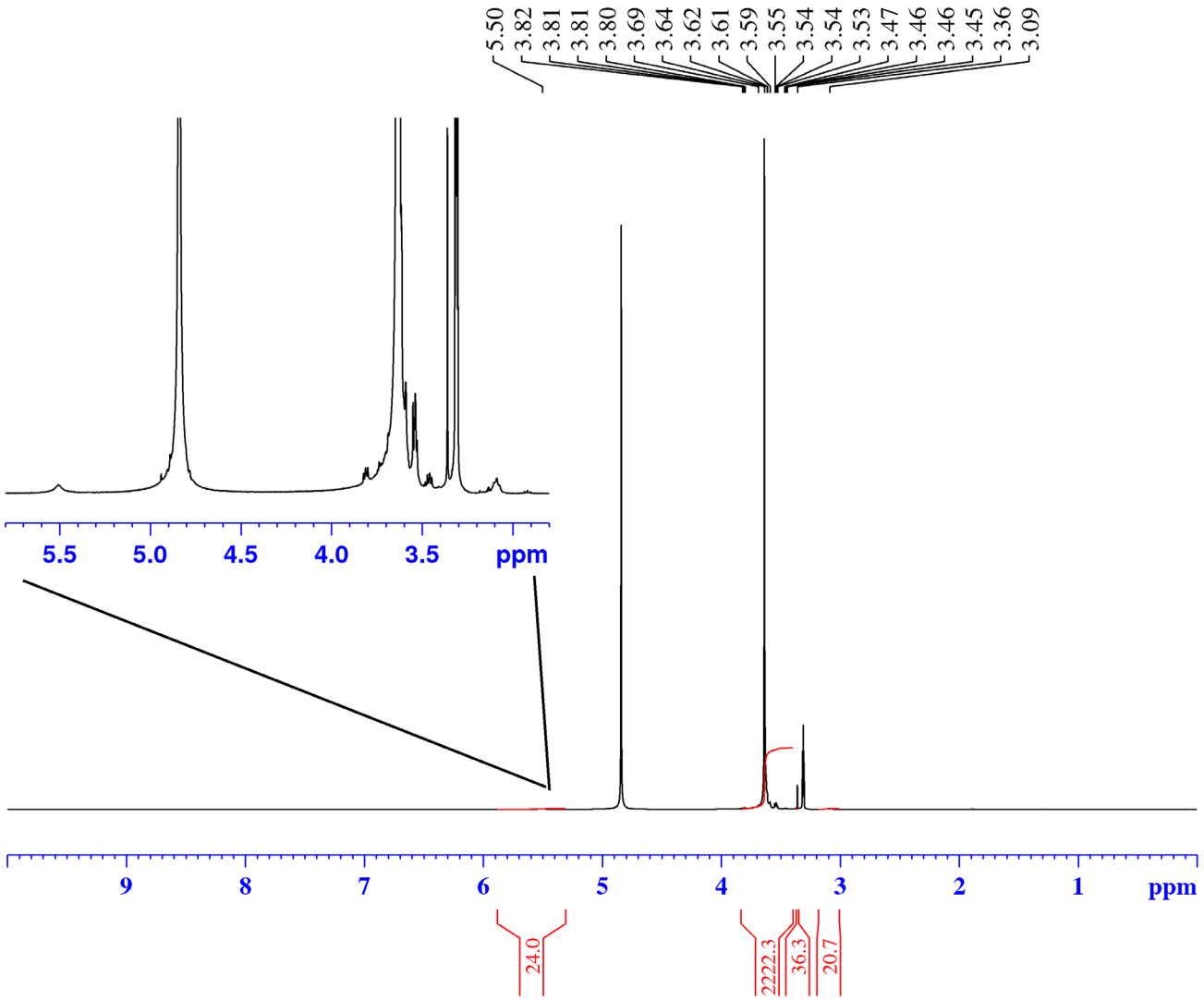
F2 - Acquisition Parameters
Date_ 20160209
Time 19.33
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

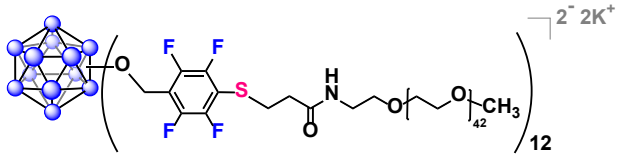


Current Data Parameters
NAME G1 PEG2000 0211 0208 MeOD
EXPNO 100
PROCNO 1

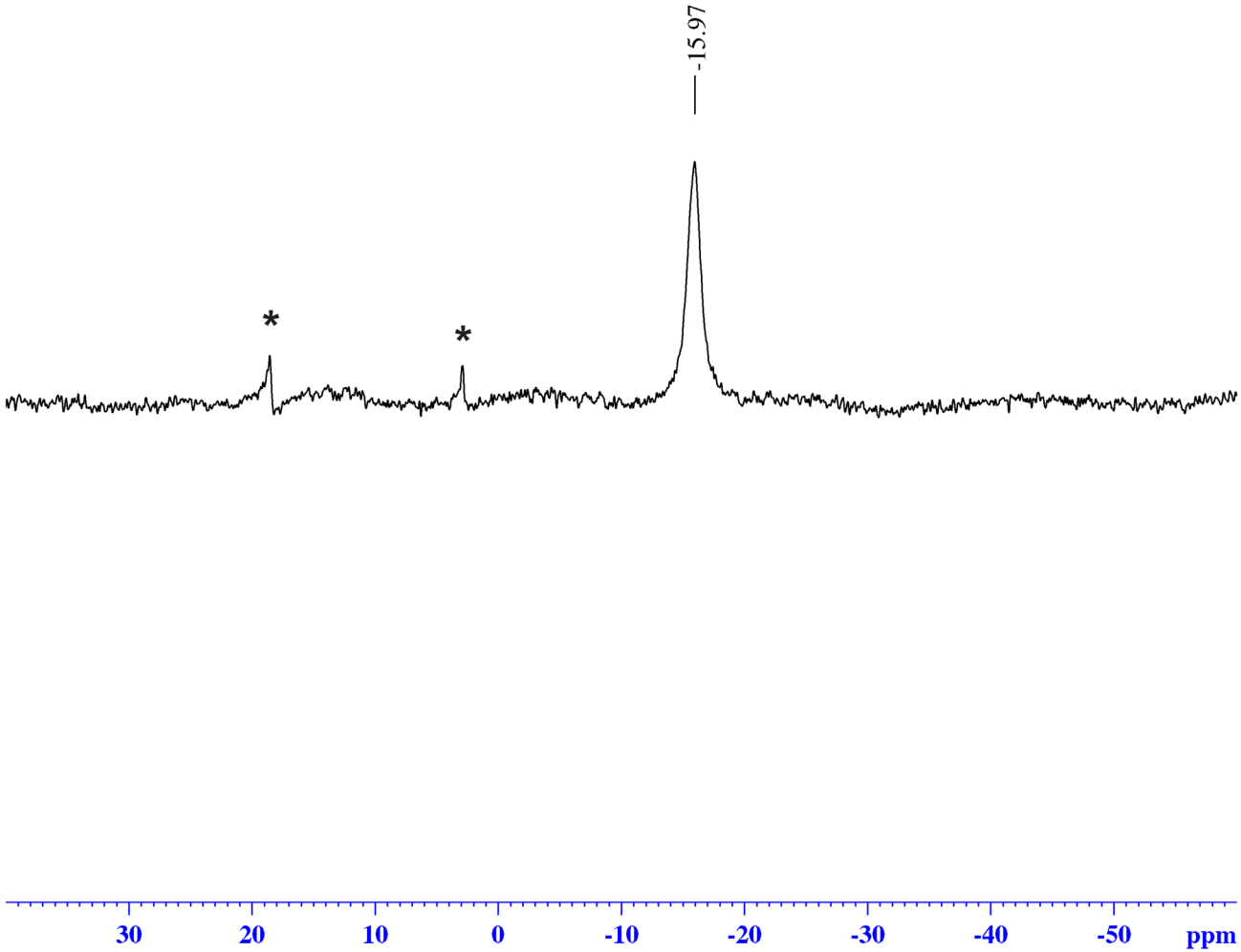
F2 - Acquisition Parameters
Date_ 20160216
Time 21.55
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR



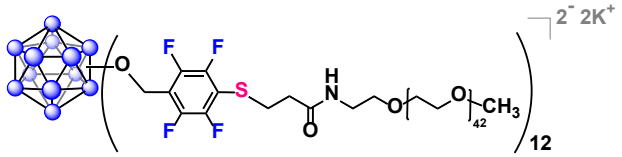
Current Data Parameters
NAME G1 PEG2000 0211 0208 MeOD
EXPNO 102
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160212
Time 13.59
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

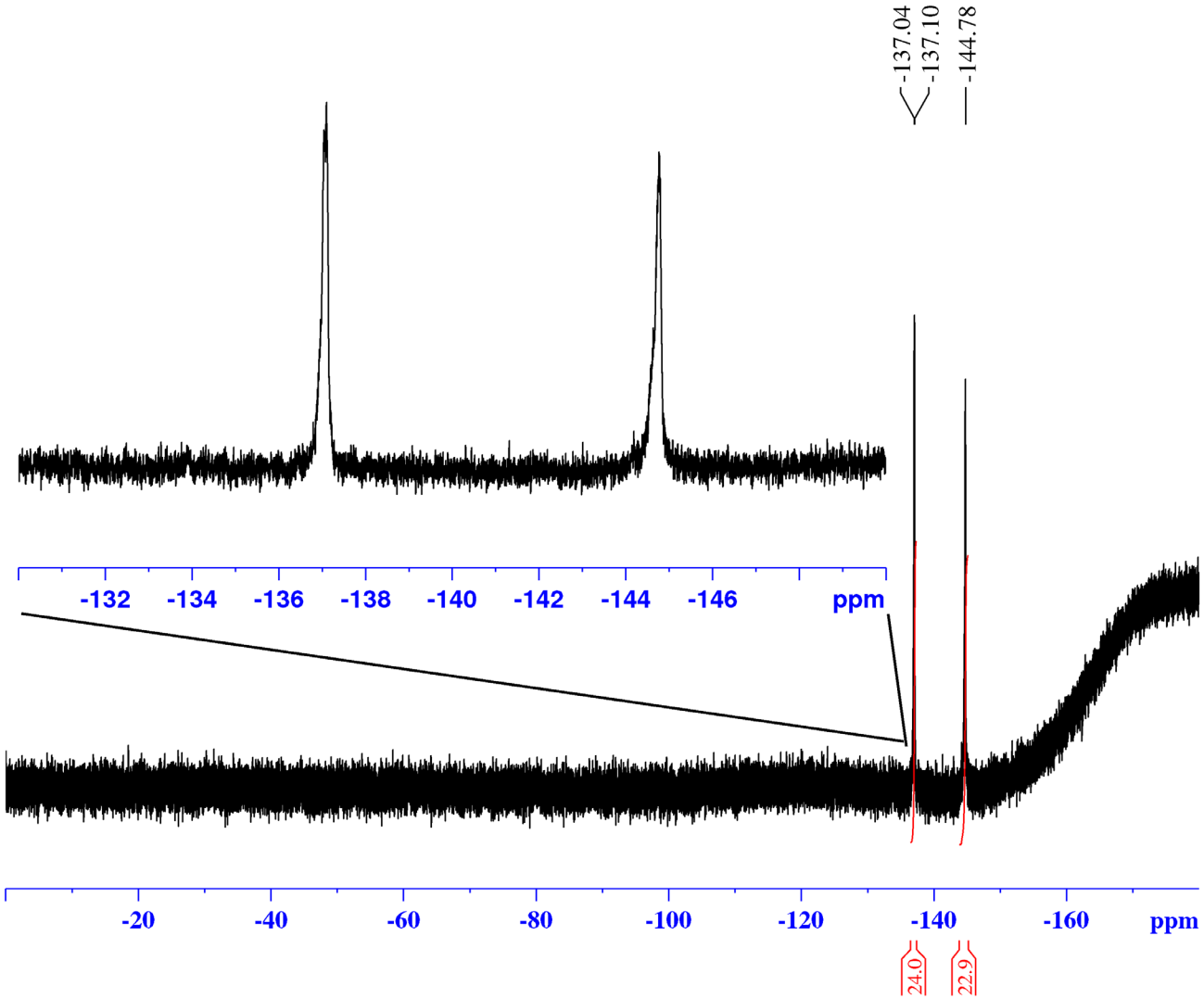
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

* These peaks correspond to small impurities - boric acid and borates.



^{19}F NMR

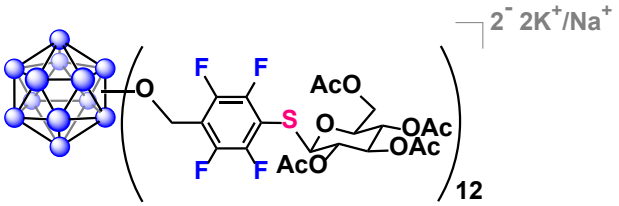


Current Data Parameters
NAME G1 PEG2000 0211 0208 MeOD
EXPNO 101
PROCNO 1

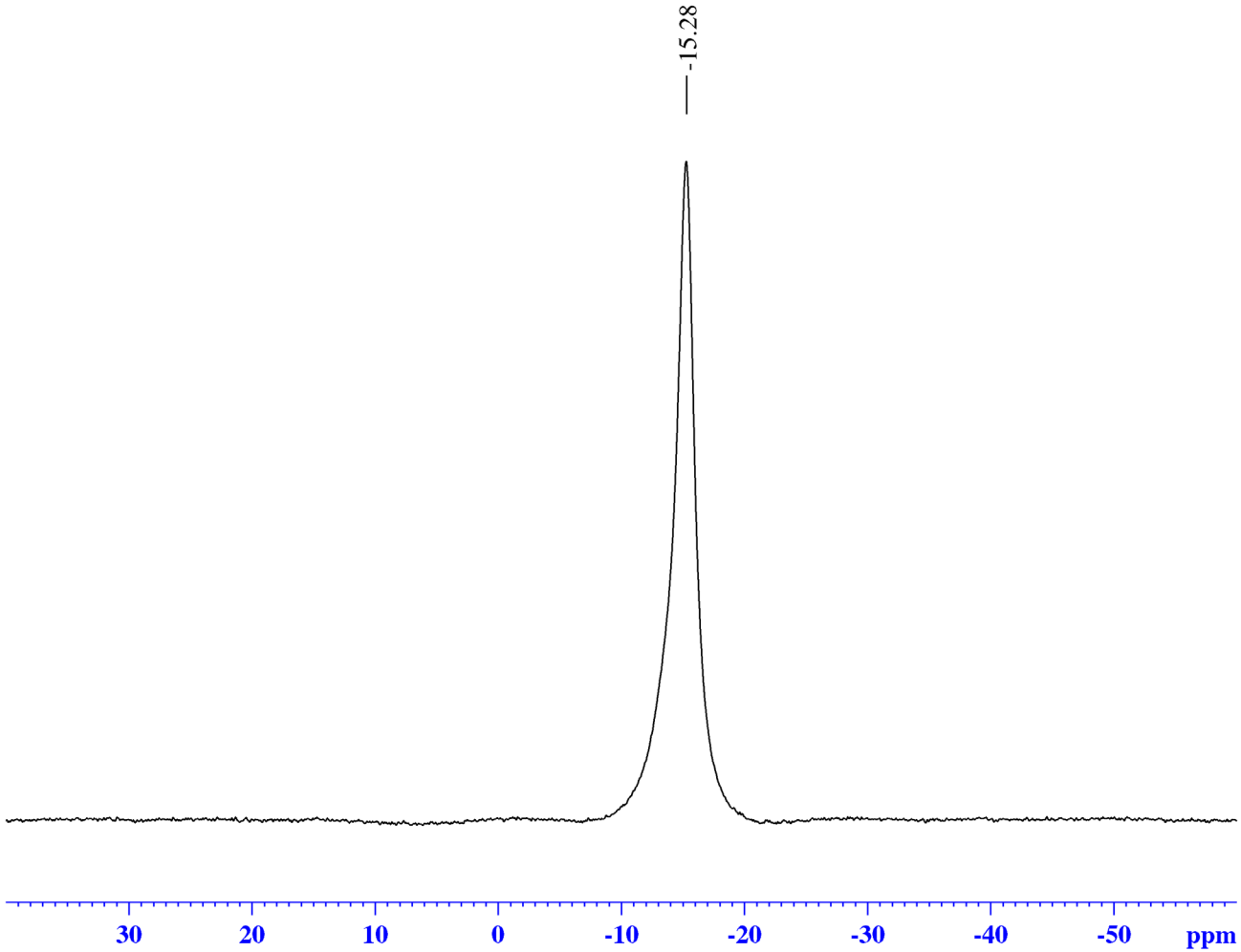
F2 - Acquisition Parameters
Date_ 20160212
Time 14.03
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



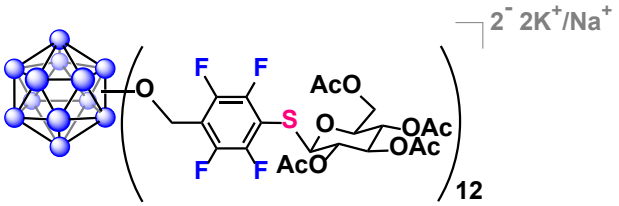
in situ ^{11}B NMR



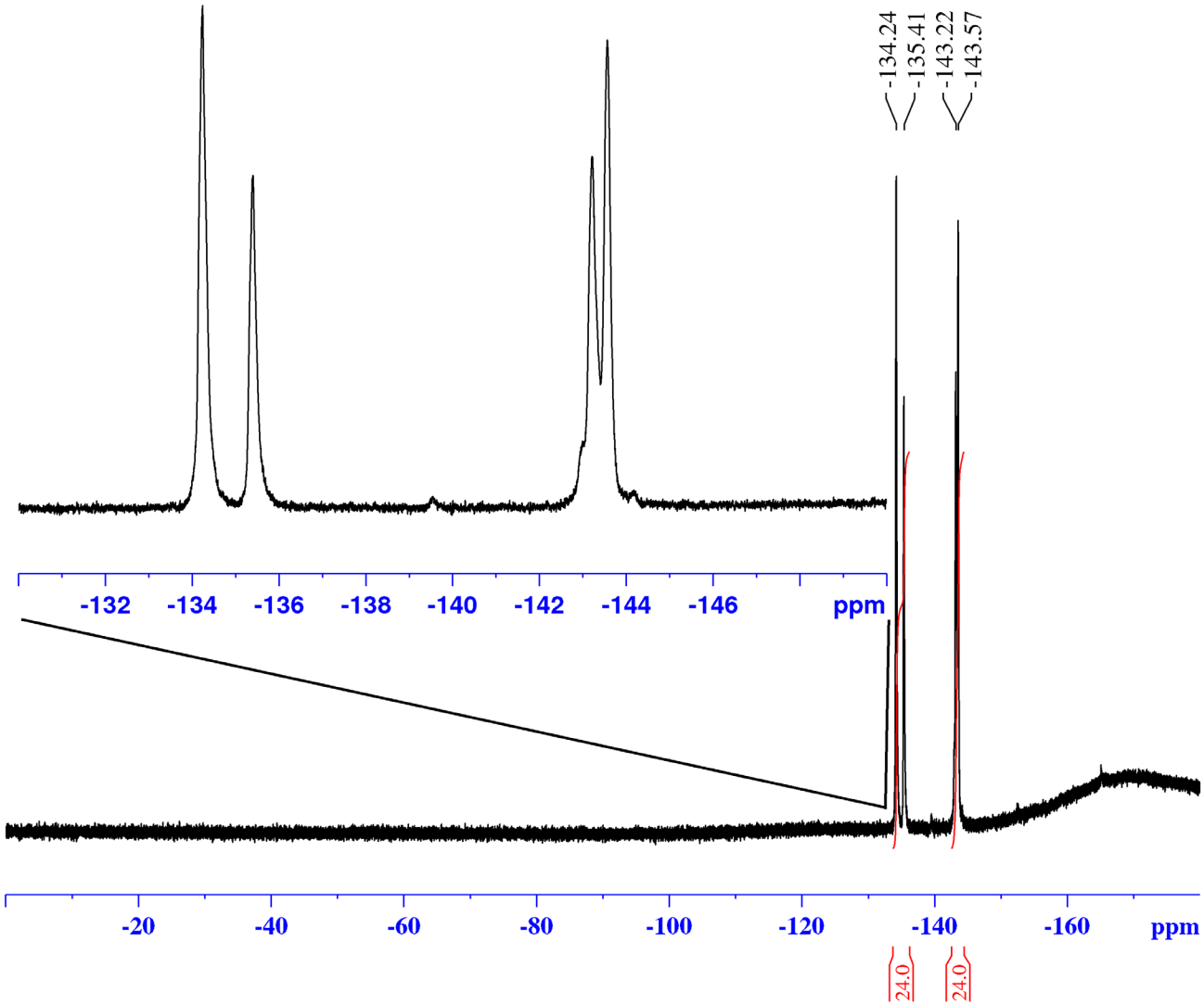
Current Data Parameters
NAME 0308
EXPNO 71
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160308
Time 15.42 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

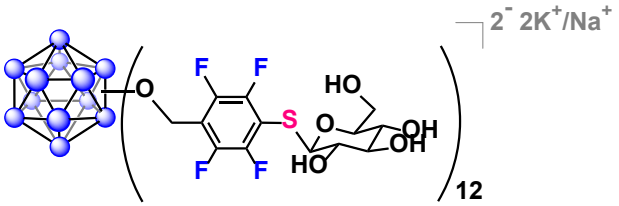


Current Data Parameters
NAME 0308
EXPNO 70
PROCNO 1

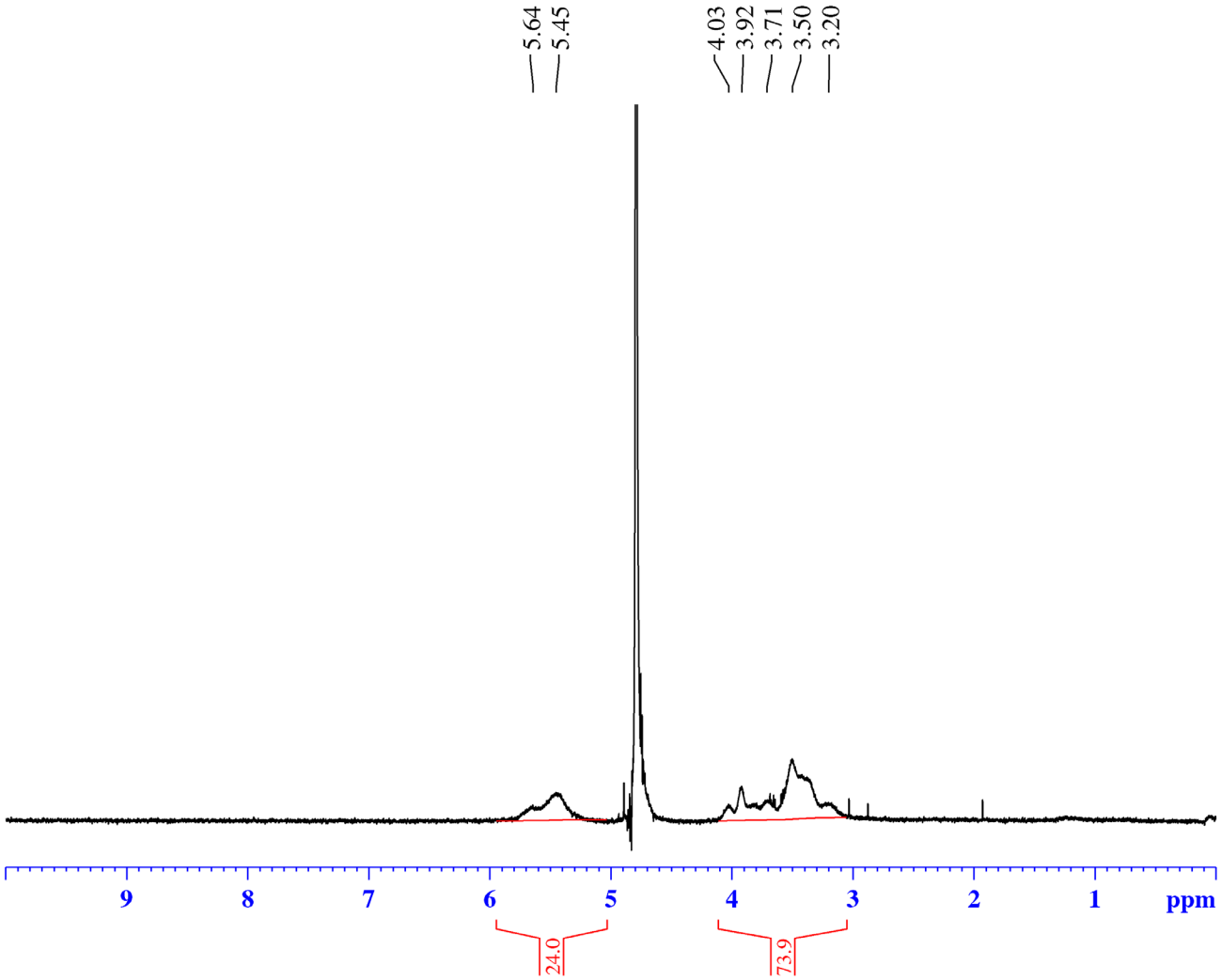
F2 - Acquisition Parameters
Date_ 20160308
Time 15.39 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 1.144409 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

Split peaks are due to the restricted rotational conformations of the molecule.[9]



^{1}H NMR

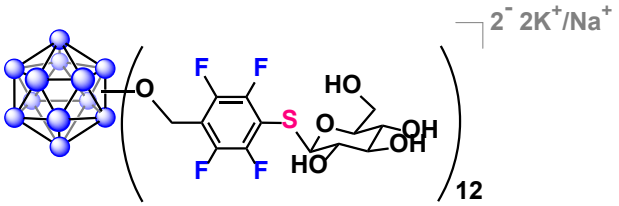


Current Data Parameters
NAME G1 Glc 2 0711 0307 D2O
EXPNO 202
PROCNO 1

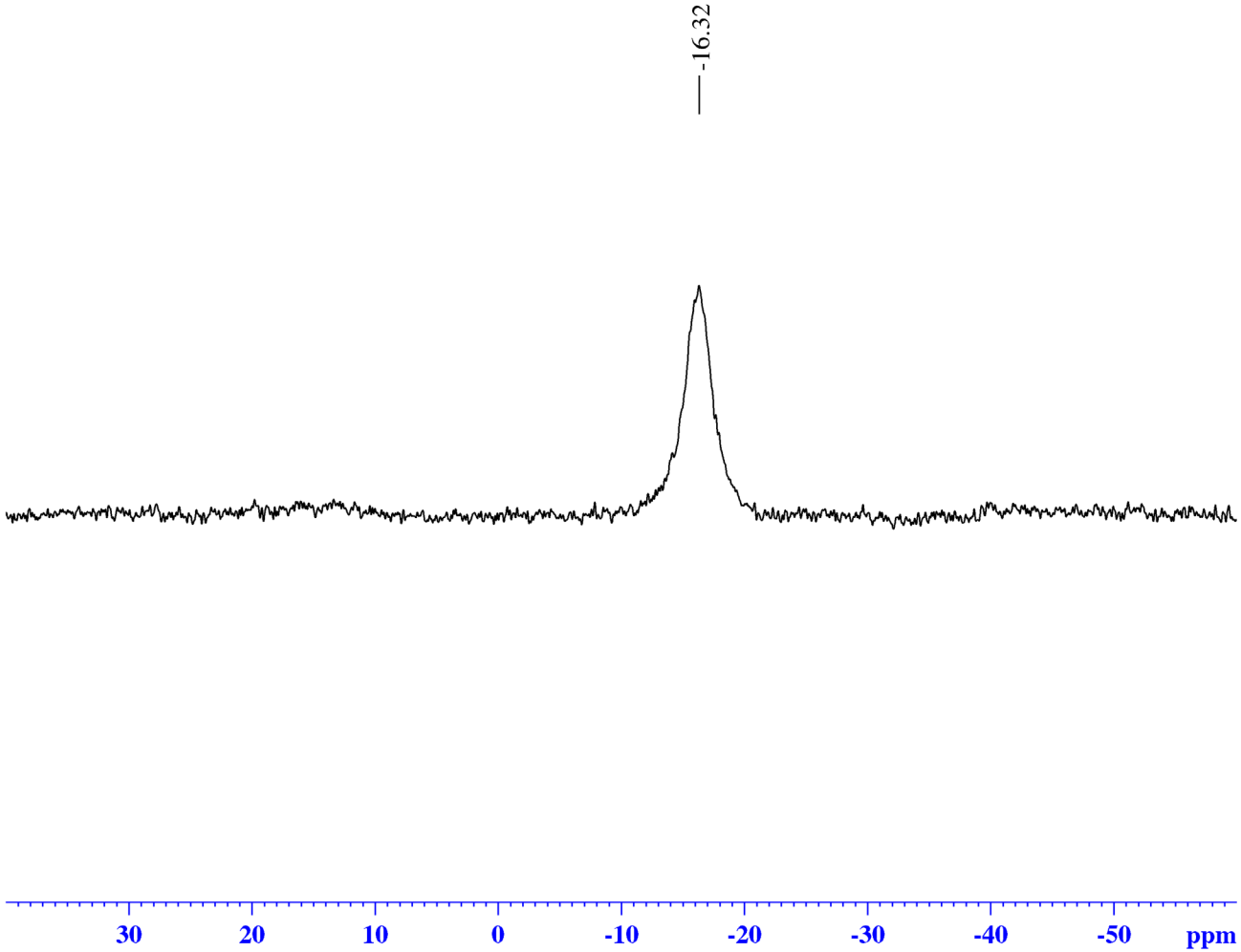
F2 - Acquisition Parameters
Date_ 20160713
Time 20.32
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT D2O
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1299638 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

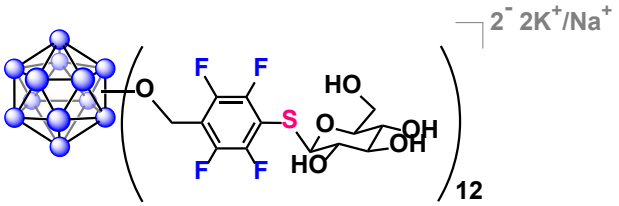


Current Data Parameters
NAME G1 Glc 2 0711 0307 D2O
EXPNO 200
PROCNO 1

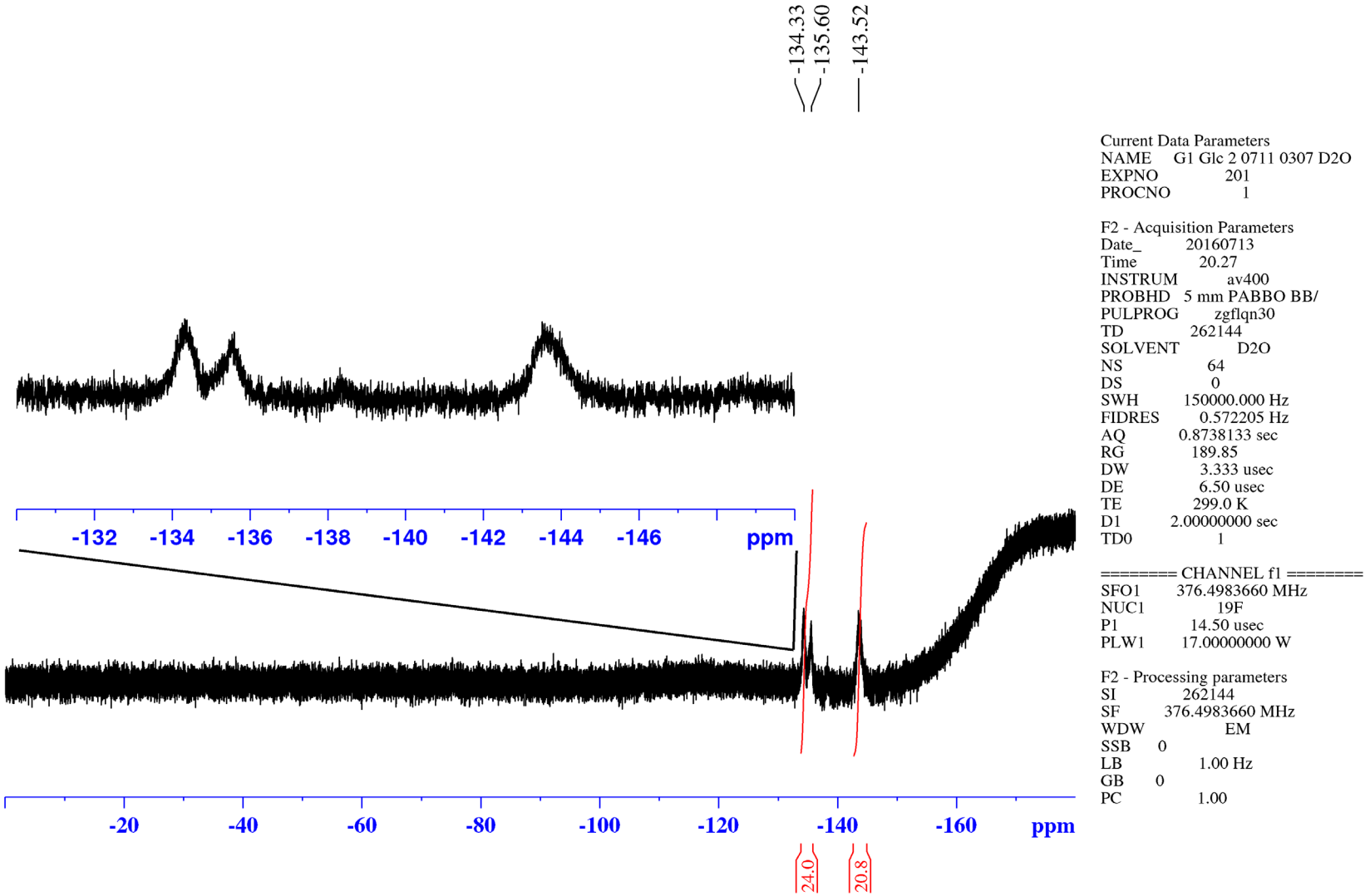
F2 - Acquisition Parameters
Date_ 20160713
Time 20.23
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT D2O
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR



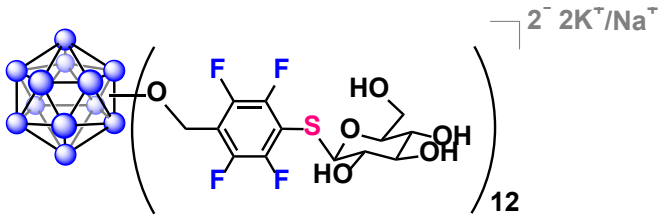
Current Data Parameters
NAME G1 Glc 2 0711 0307 D2O
EXPNO 201
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160713
Time 20.27
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT D2O
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

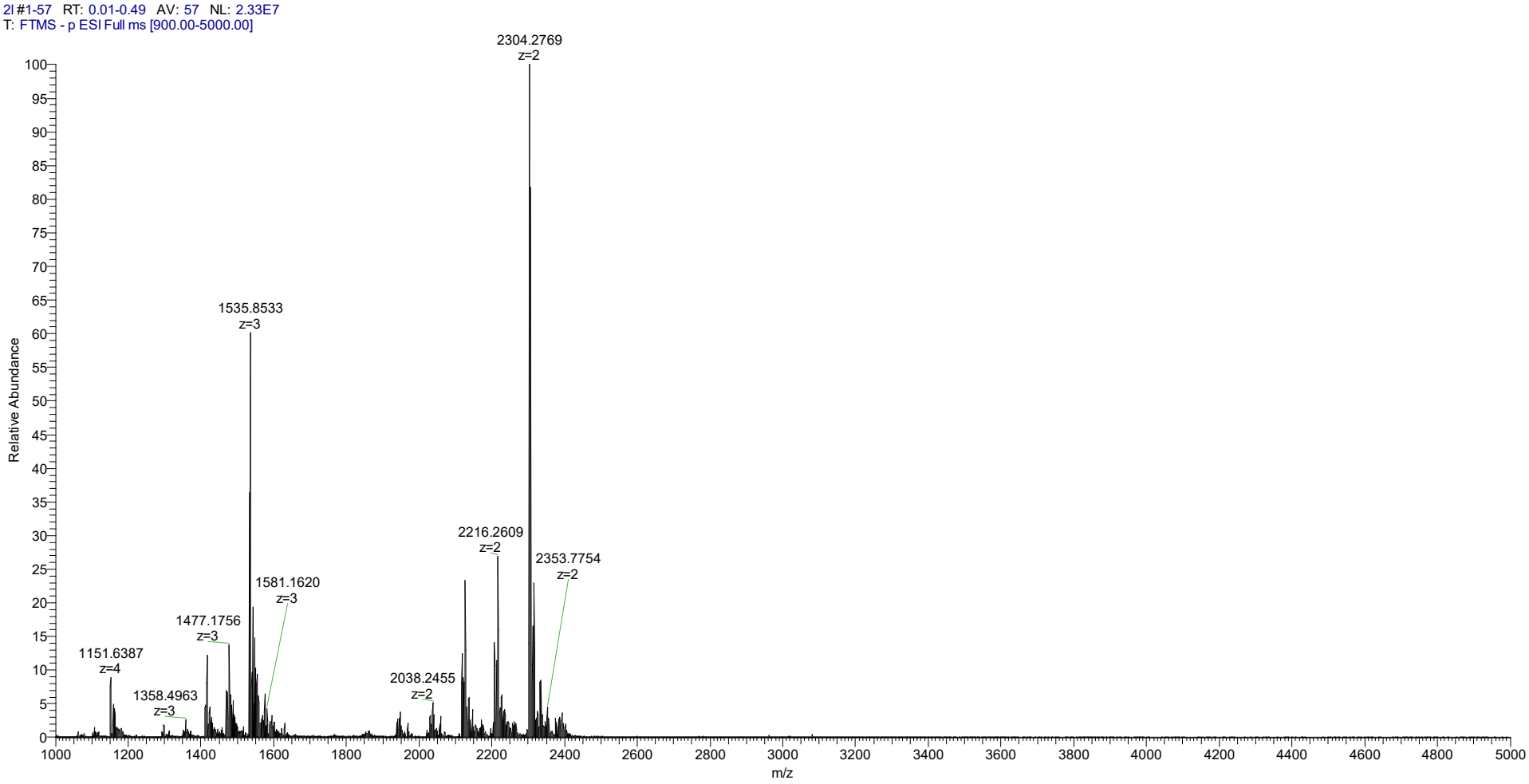
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

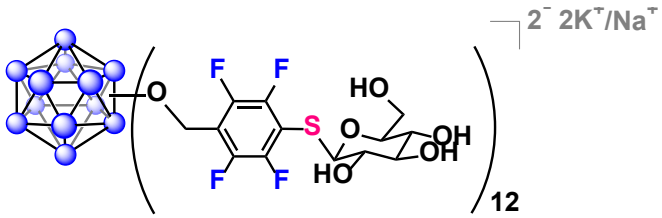
F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

Broad, split peaks are due to the restricted rotational conformations of the molecule.[9]

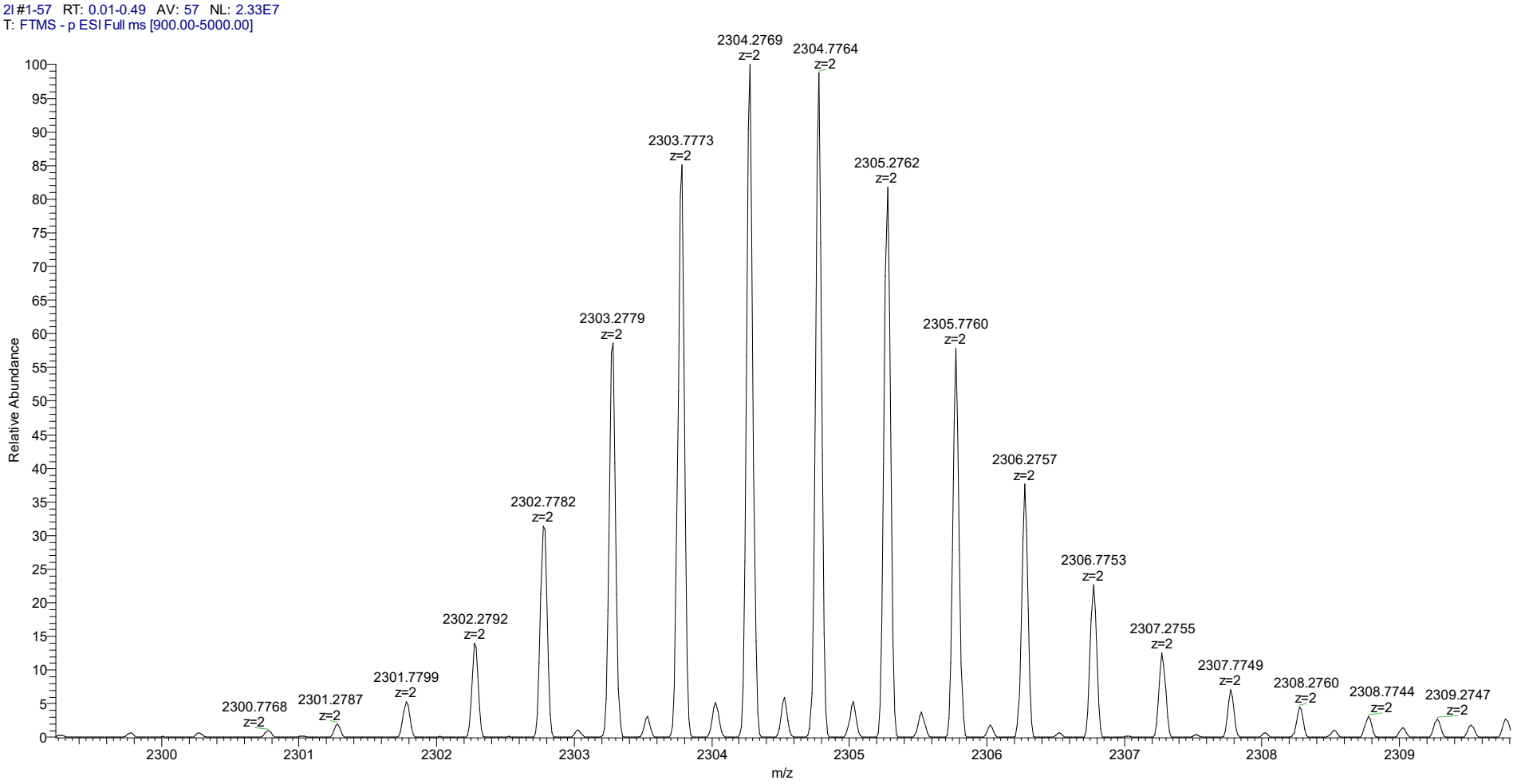


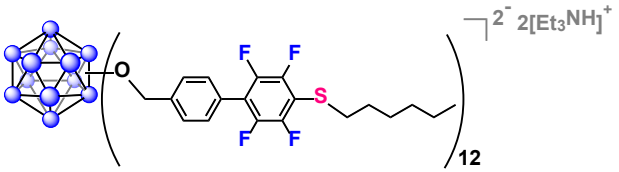
Q Exactive
High-Res Mass Spec



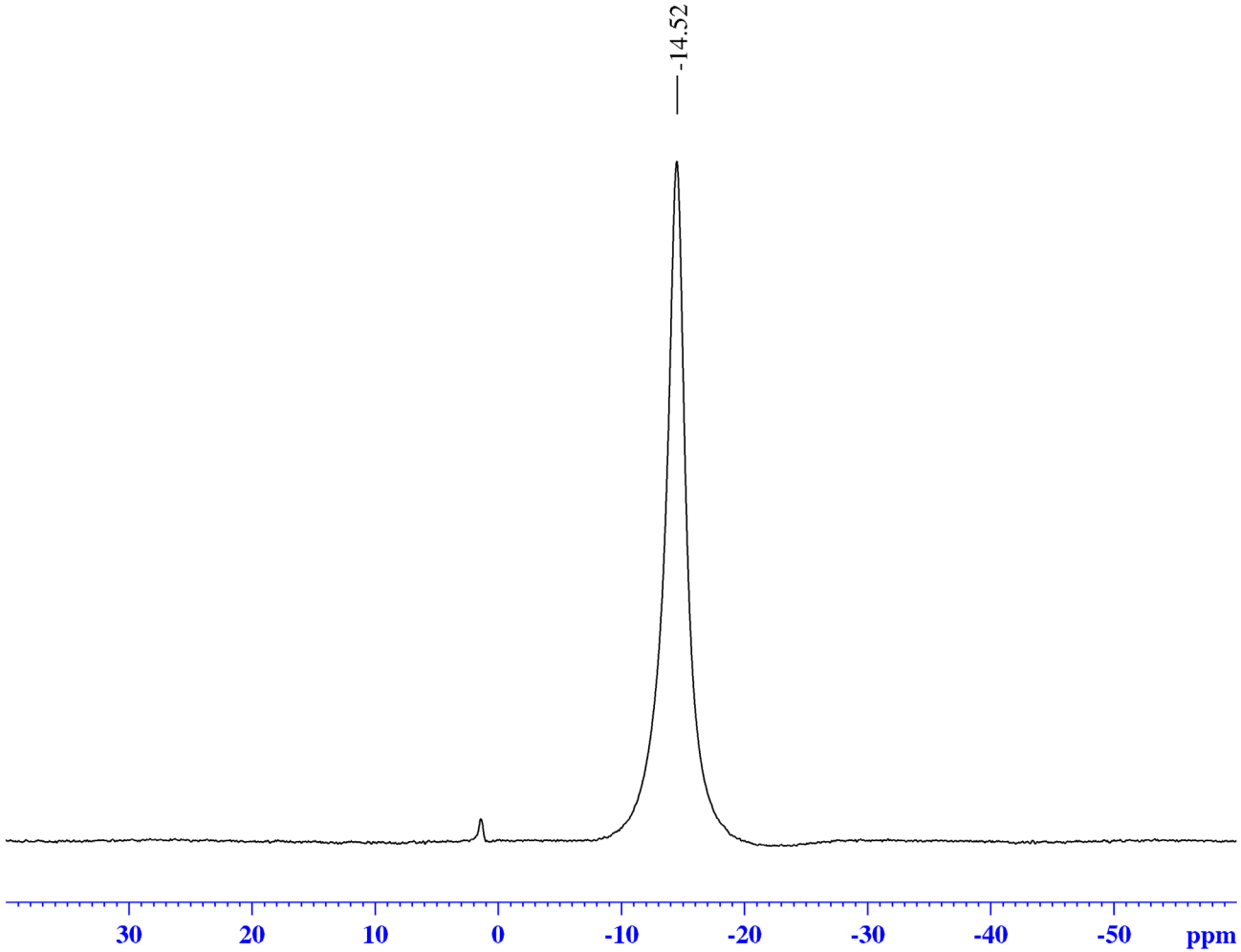


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

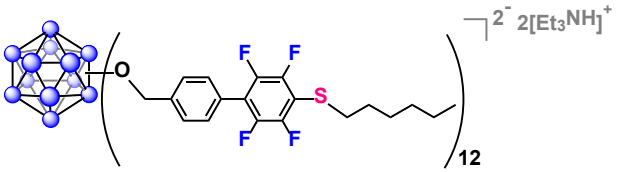


Current Data Parameters
NAME 0119
EXPNO 151
PROCNO 1

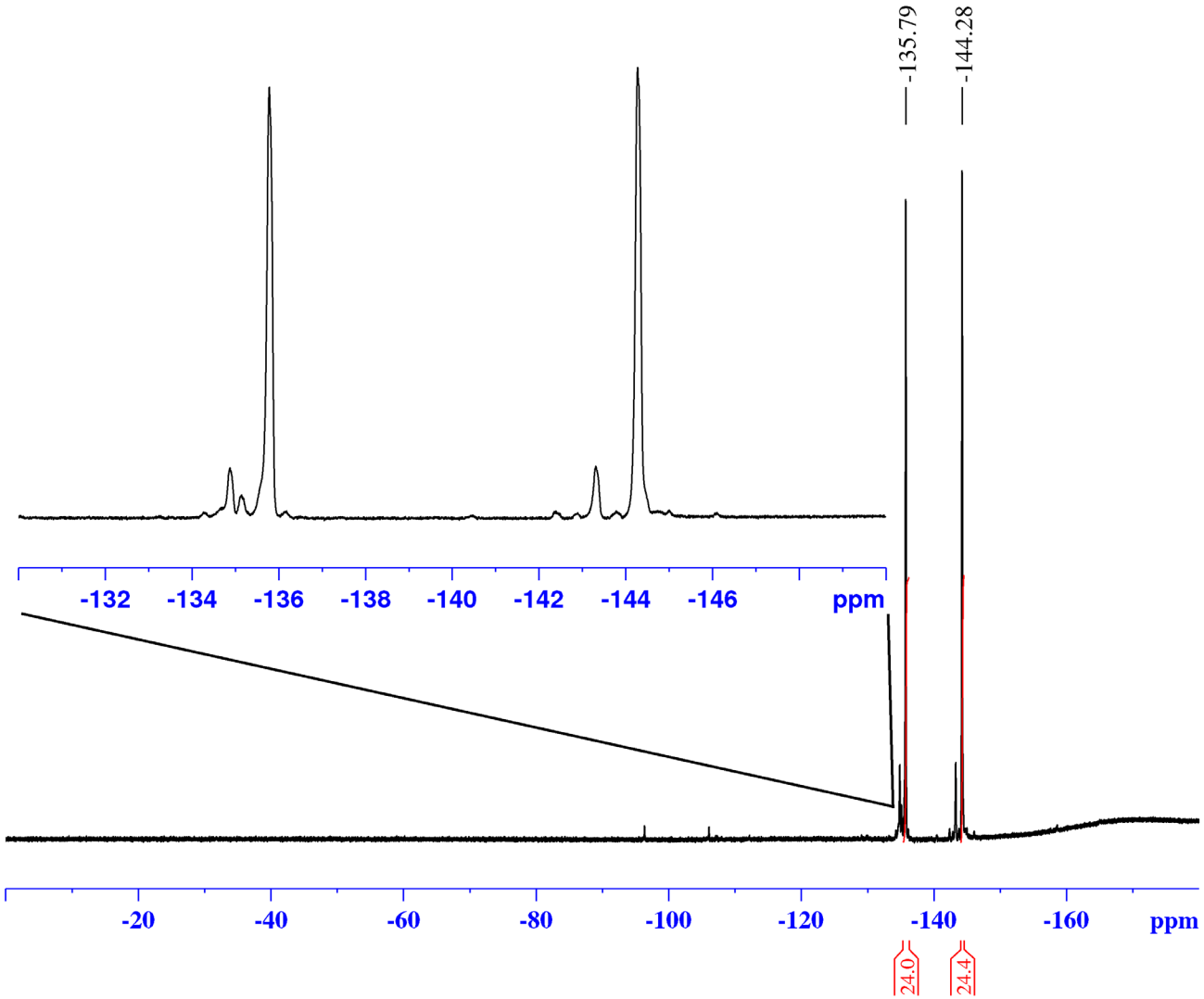
F2 - Acquisition Parameters
Date_ 20160119
Time 19.56
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR



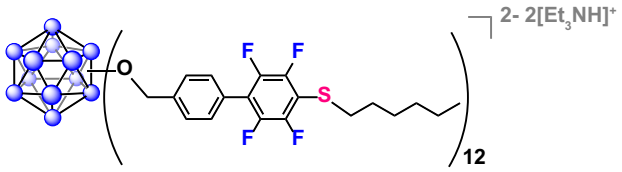
Current Data Parameters
NAME 0119
EXPNO 150
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160119
Time 19.53
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

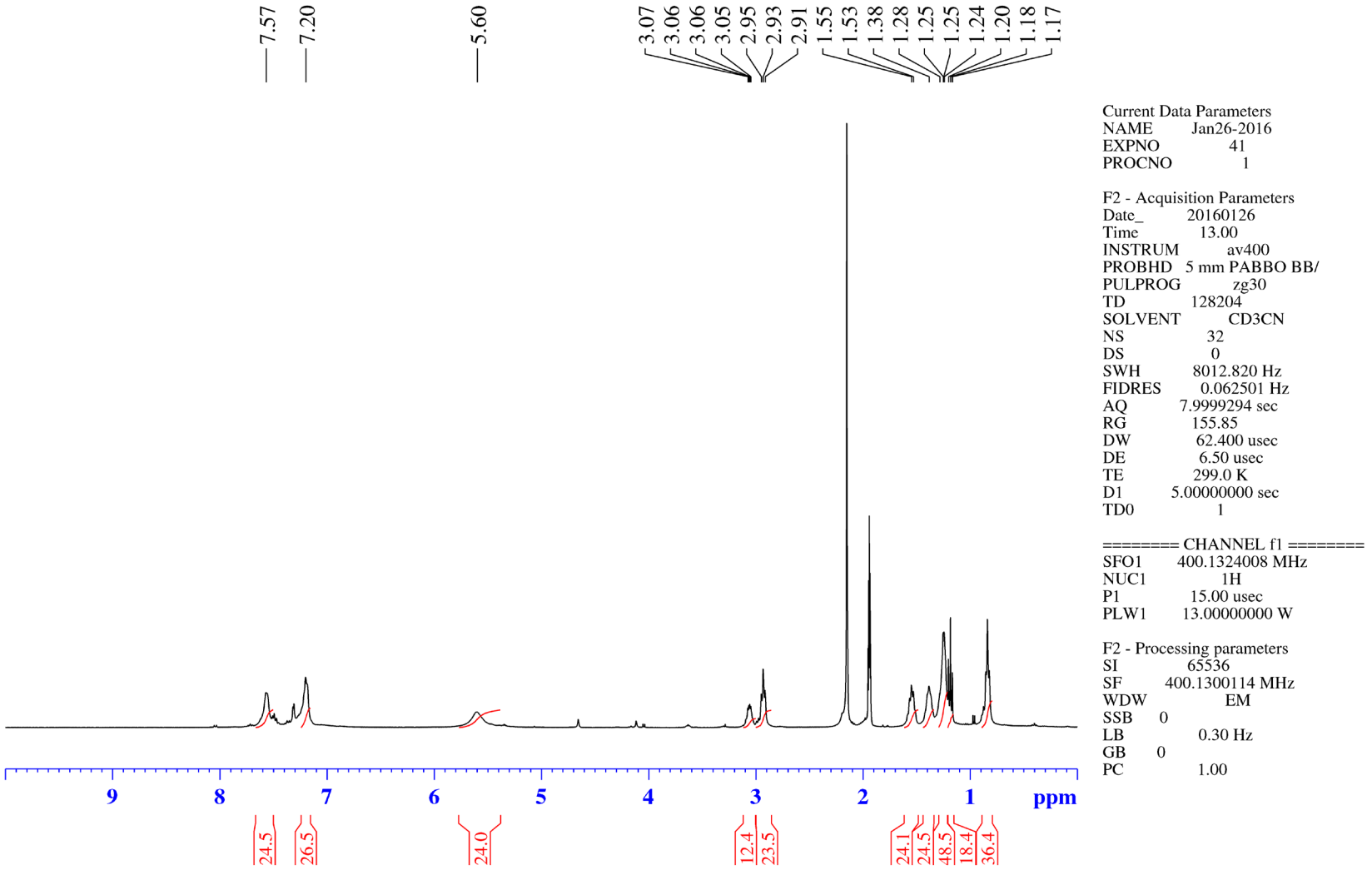
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

Small impurities are present due to the commercial 1-hexanethiol used (95% pure).



^{1}H NMR

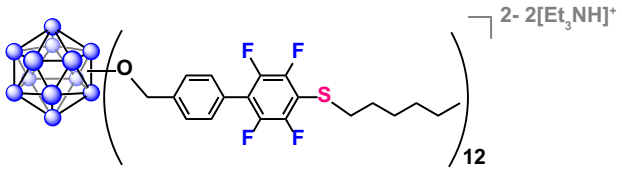


Current Data Parameters
NAME Jan26-2016
EXPNO 41
PROCNO 1

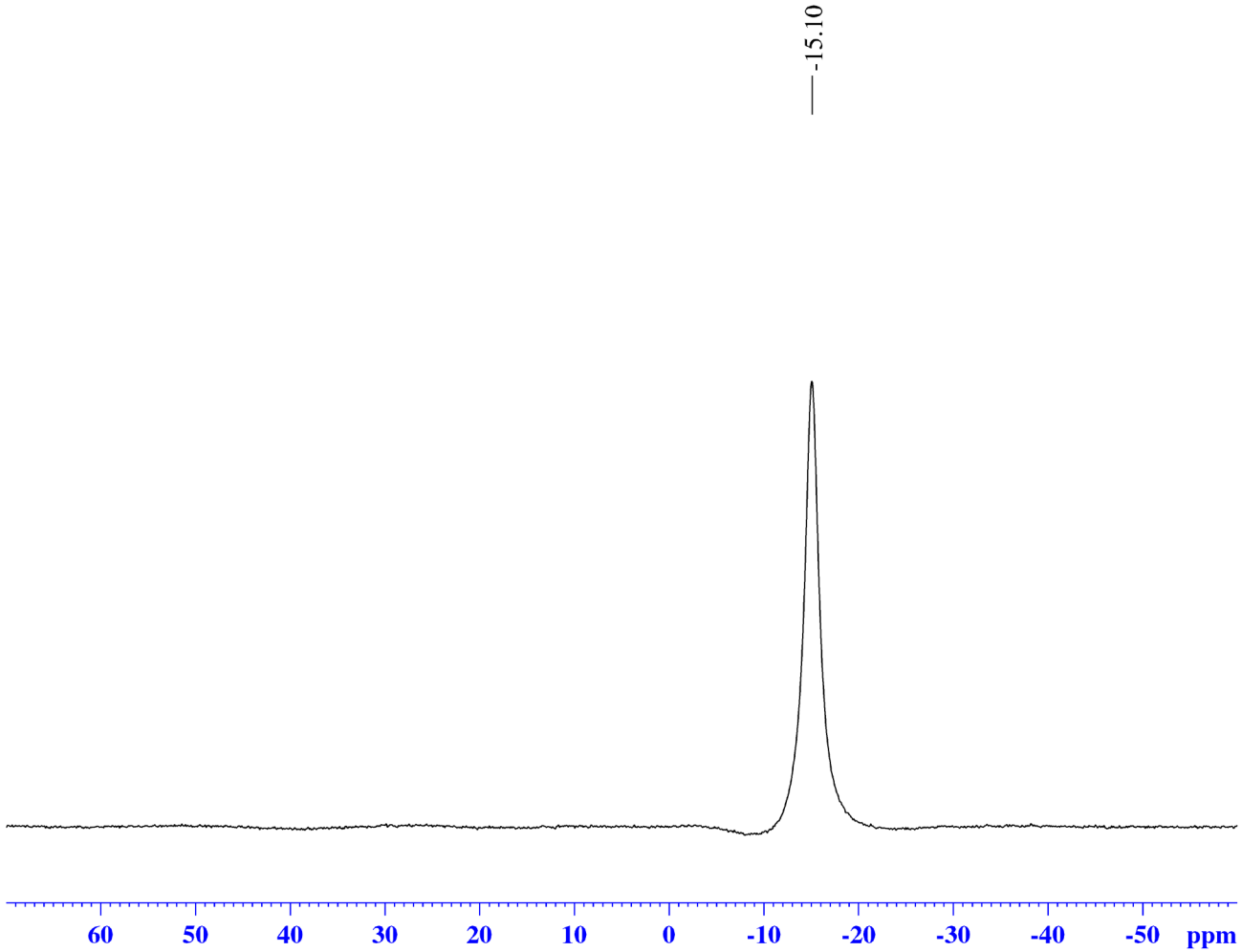
F2 - Acquisition Parameters
Date_ 20160126
Time 13.00
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 128204
SOLVENT CD3CN
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.062501 Hz
AQ 7.9999294 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300114 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B {^{1}H} NMR



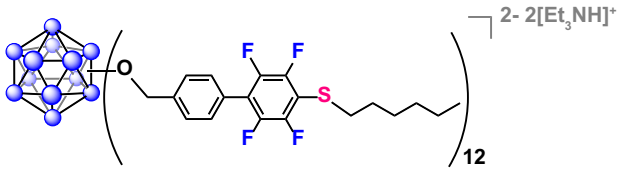
Current Data Parameters
NAME Jan26-2016
EXPNO 40
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160126
Time 12.53
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgdc.js
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.1 K
D1 0.05000000 sec
D11 0.03000000 sec
TD0 1

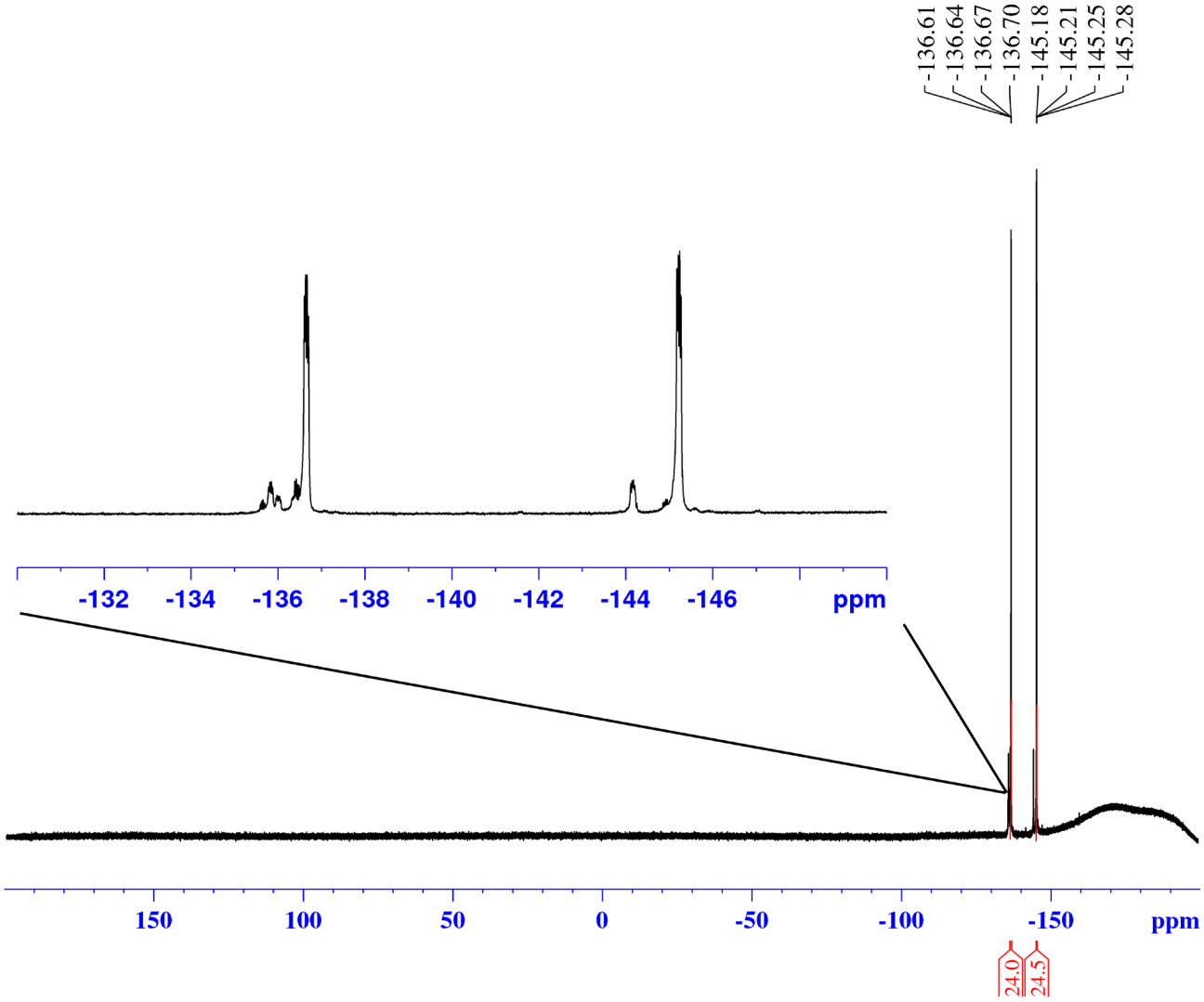
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR



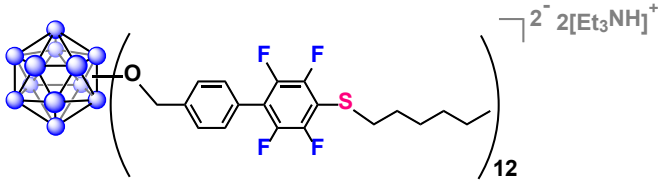
Current Data Parameters
NAME Jan26-2016
EXPNO 42
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160126
Time 13.05
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

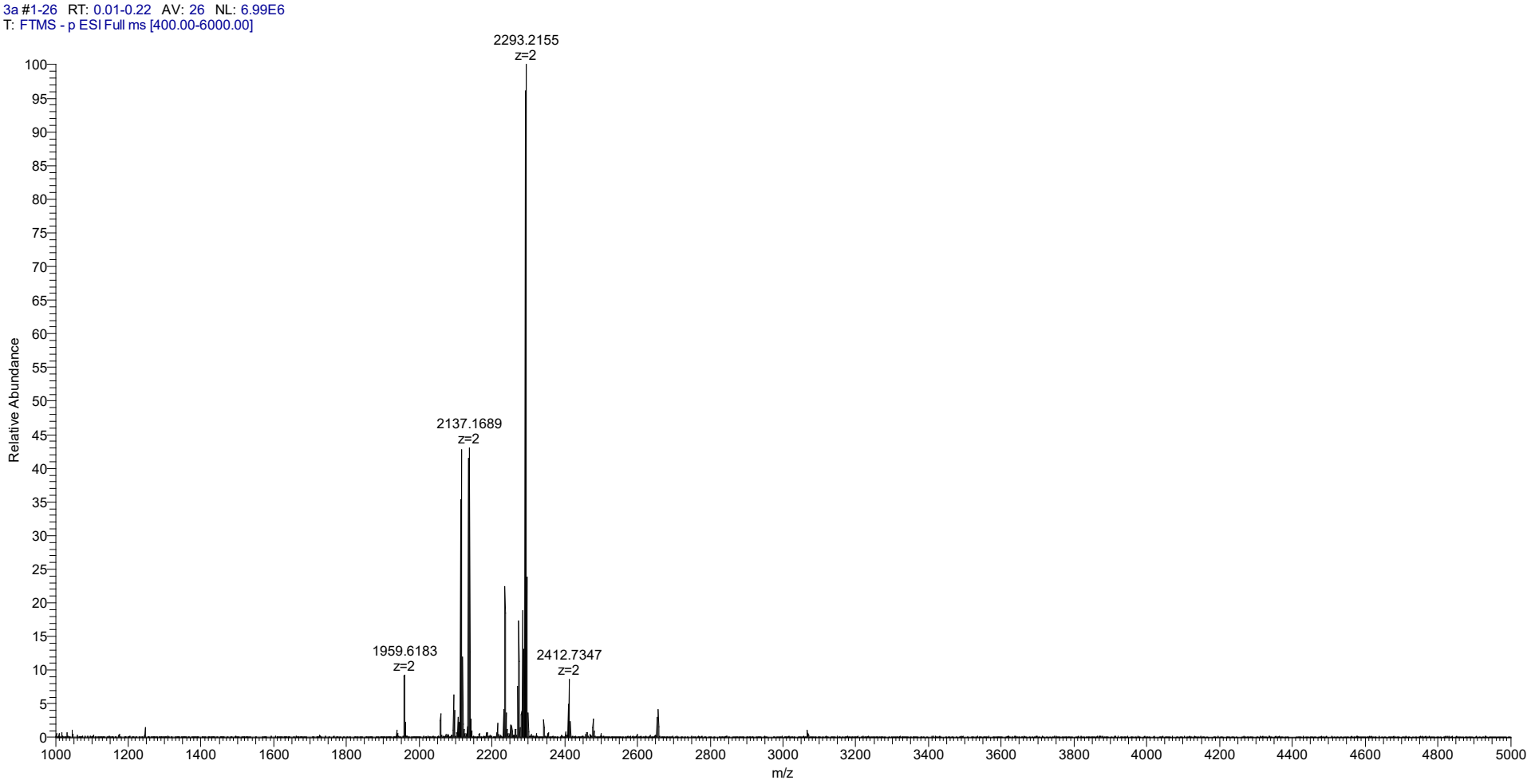
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

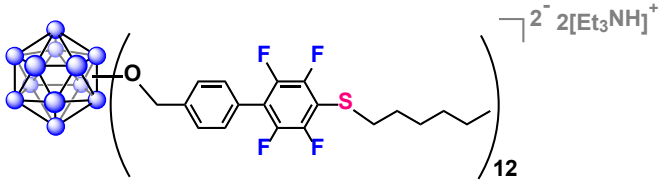
F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

Small impurities are present due to the commercial 1-hexanethiol used (95% pure).

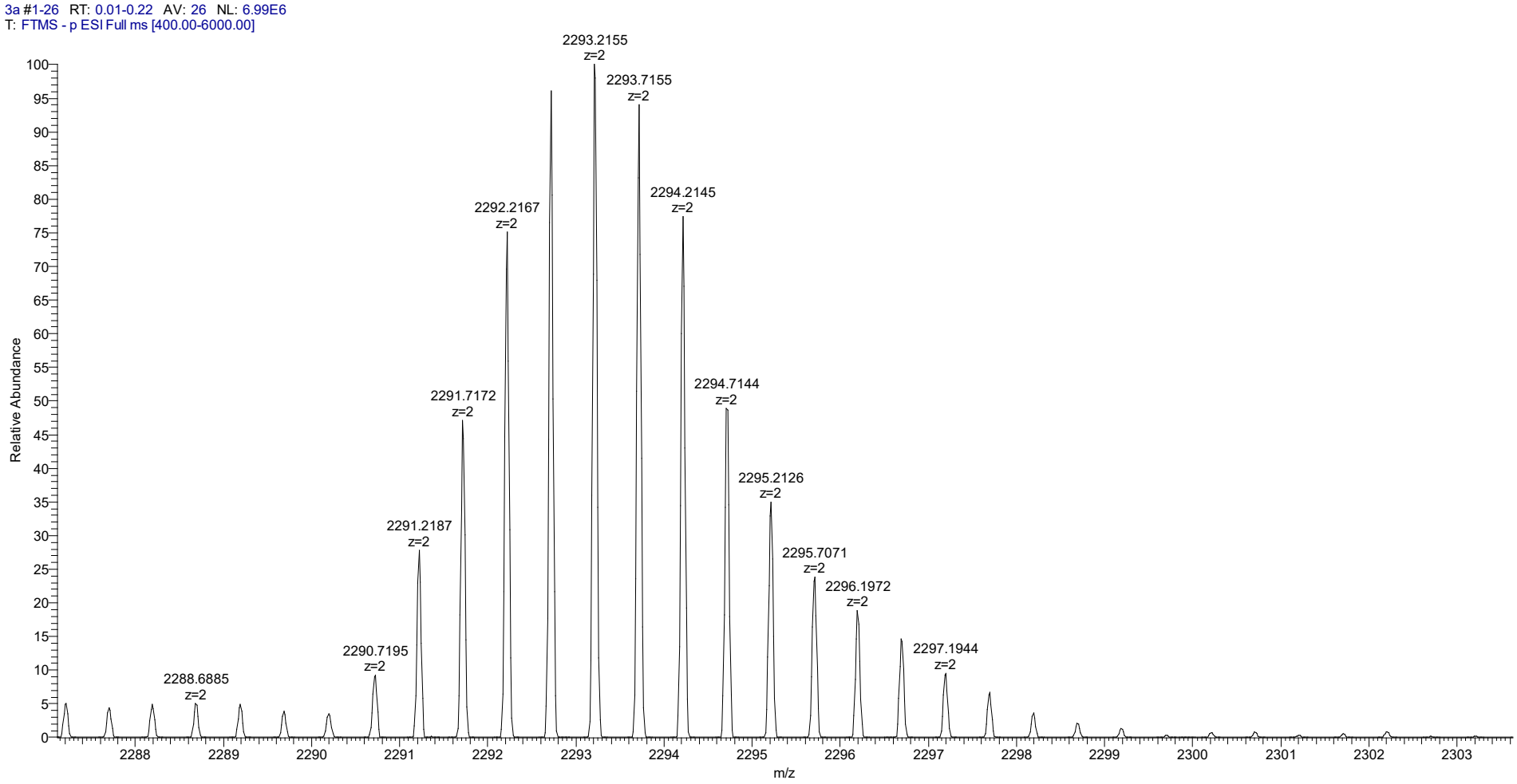


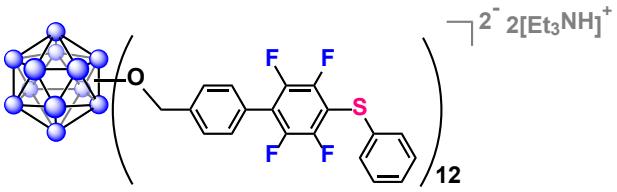
Q Exactive
High-Res Mass Spec



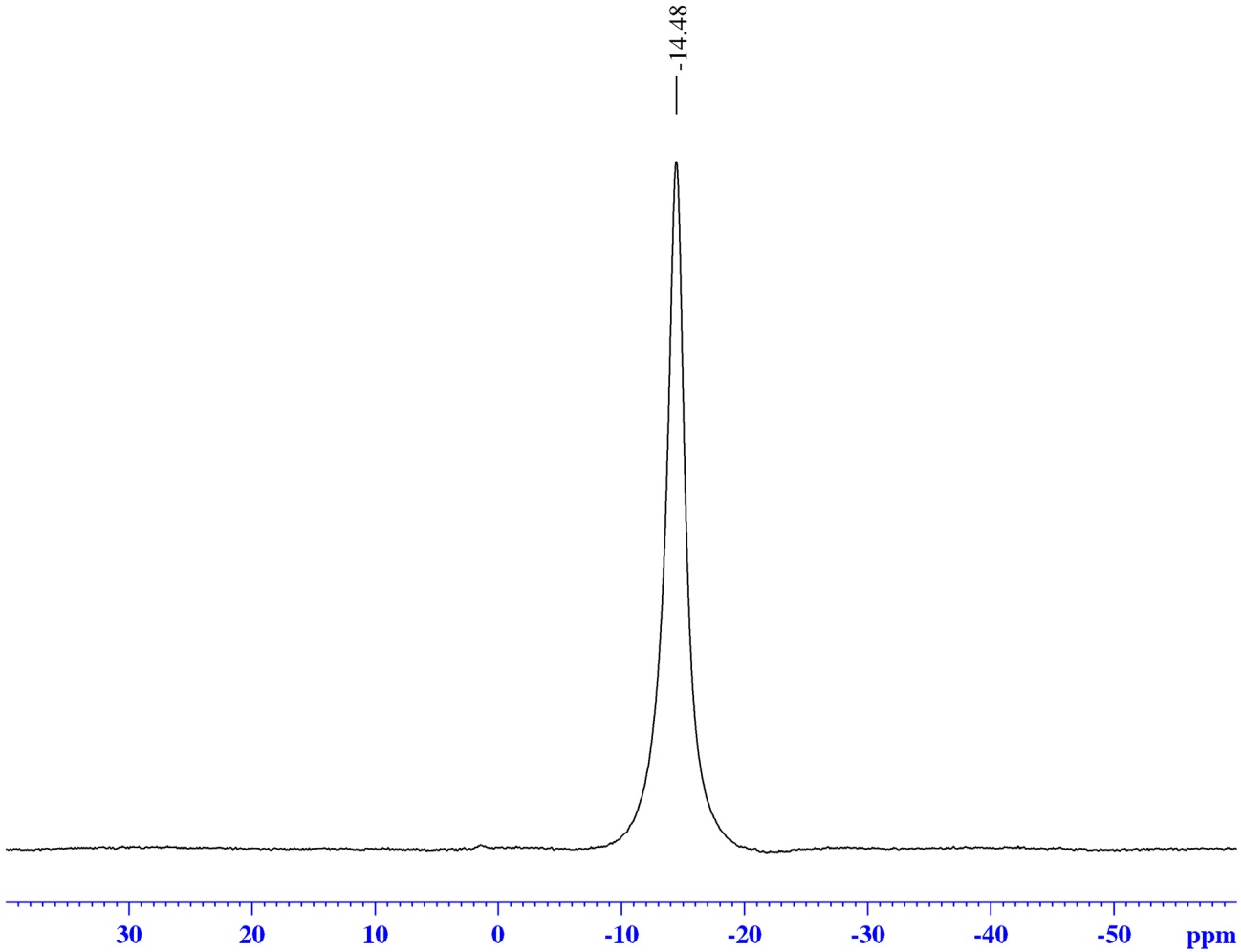


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

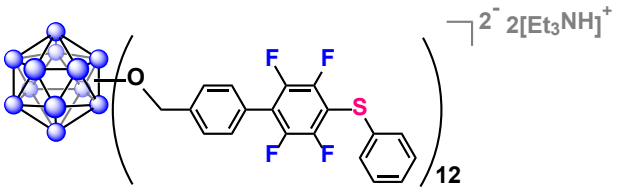


Current Data Parameters
NAME 0119
EXPNO 131
PROCNO 1

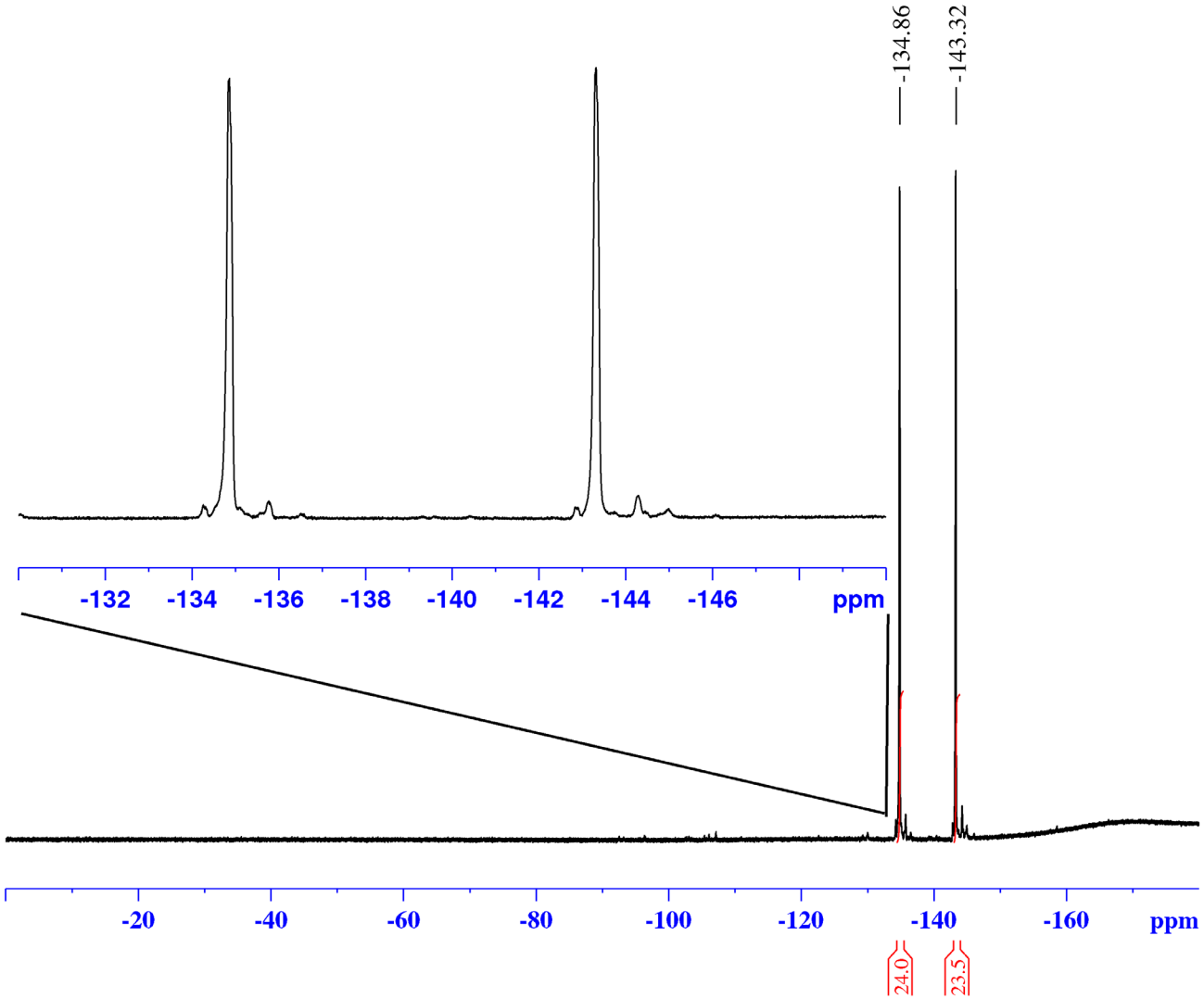
F2 - Acquisition Parameters
Date_ 20160119
Time 19.39
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

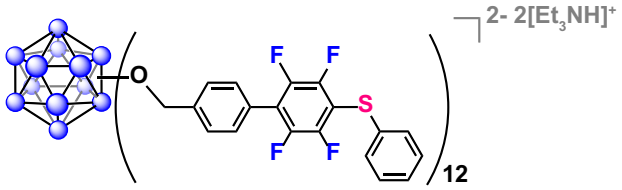


Current Data Parameters
NAME 0119
EXPNO 130
PROCNO 1

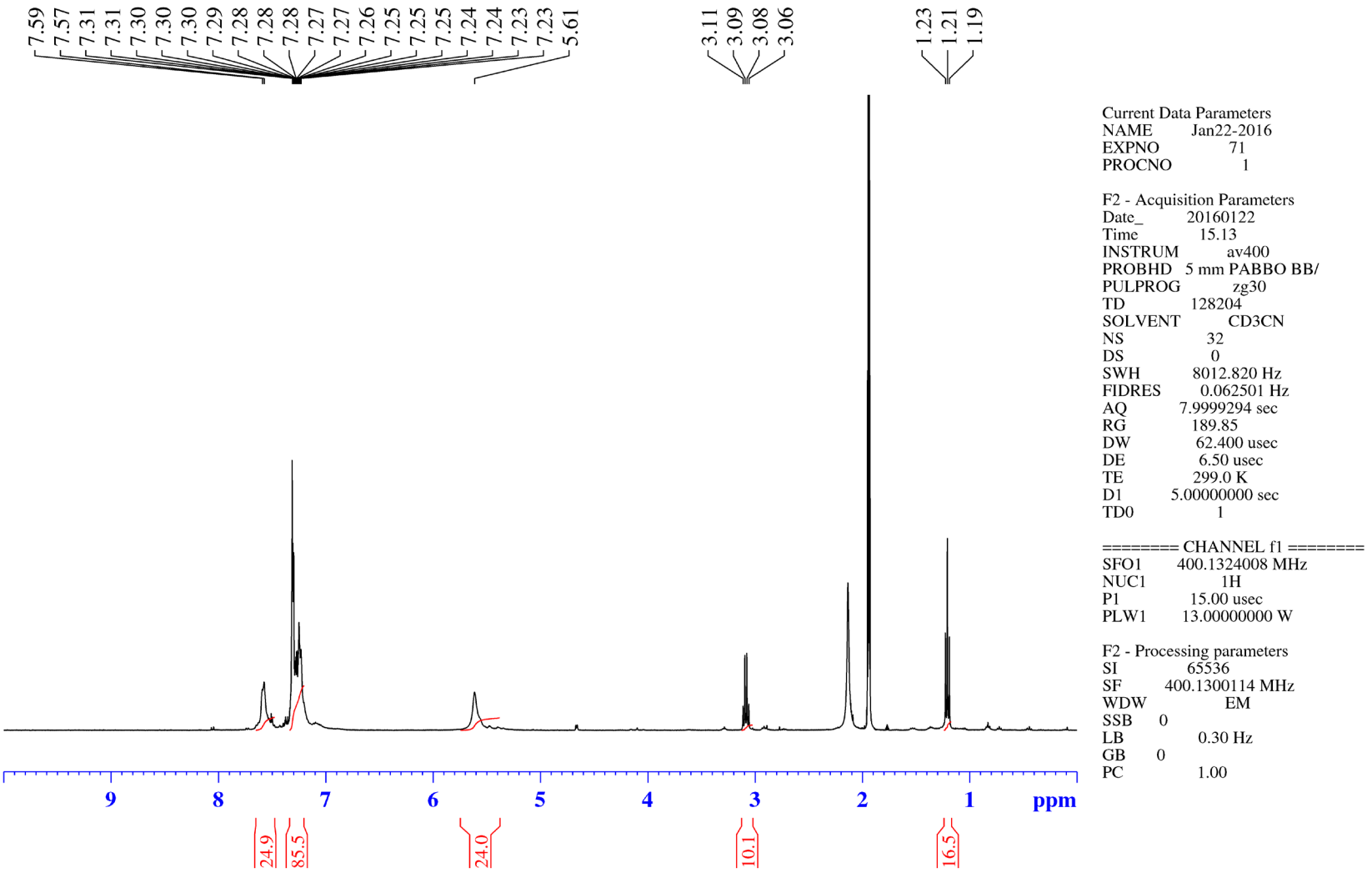
F2 - Acquisition Parameters
Date_ 20160119
Time 19.35
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

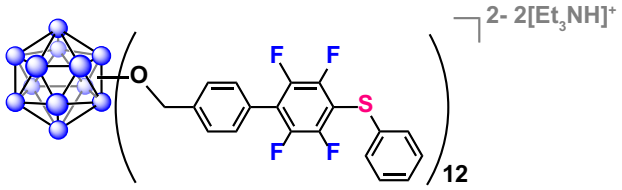


Current Data Parameters
NAME Jan22-2016
EXPNO 71
PROCNO 1

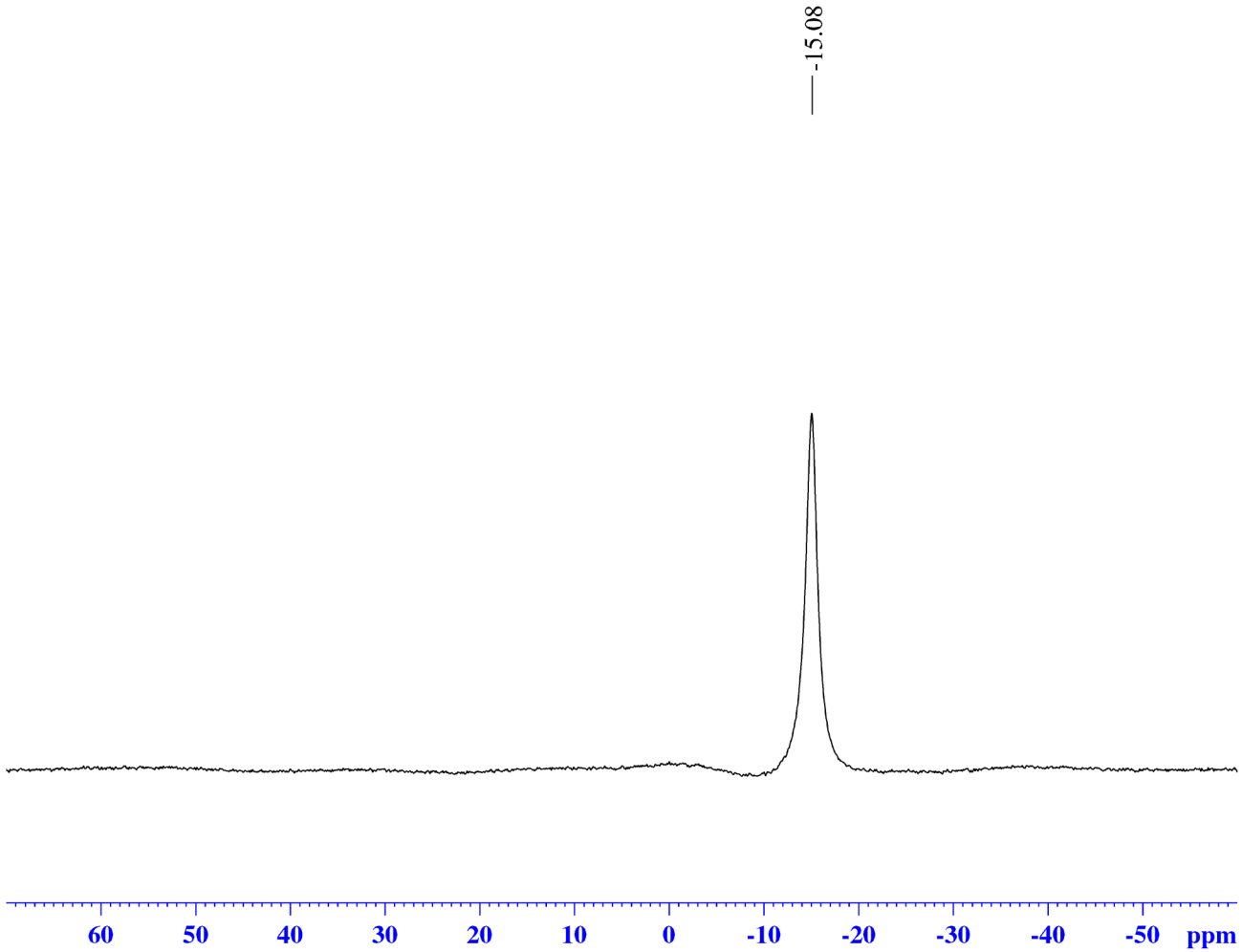
F2 - Acquisition Parameters
Date_ 20160122
Time 15.13
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 128204
SOLVENT CD3CN
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.062501 Hz
AQ 7.9999294 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300114 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B {^{1}H} NMR



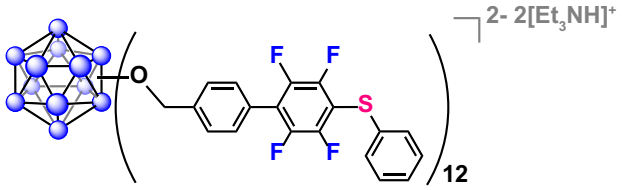
Current Data Parameters
NAME Jan22-2016
EXPNO 70
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160122
Time 15.05
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgdc.js
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

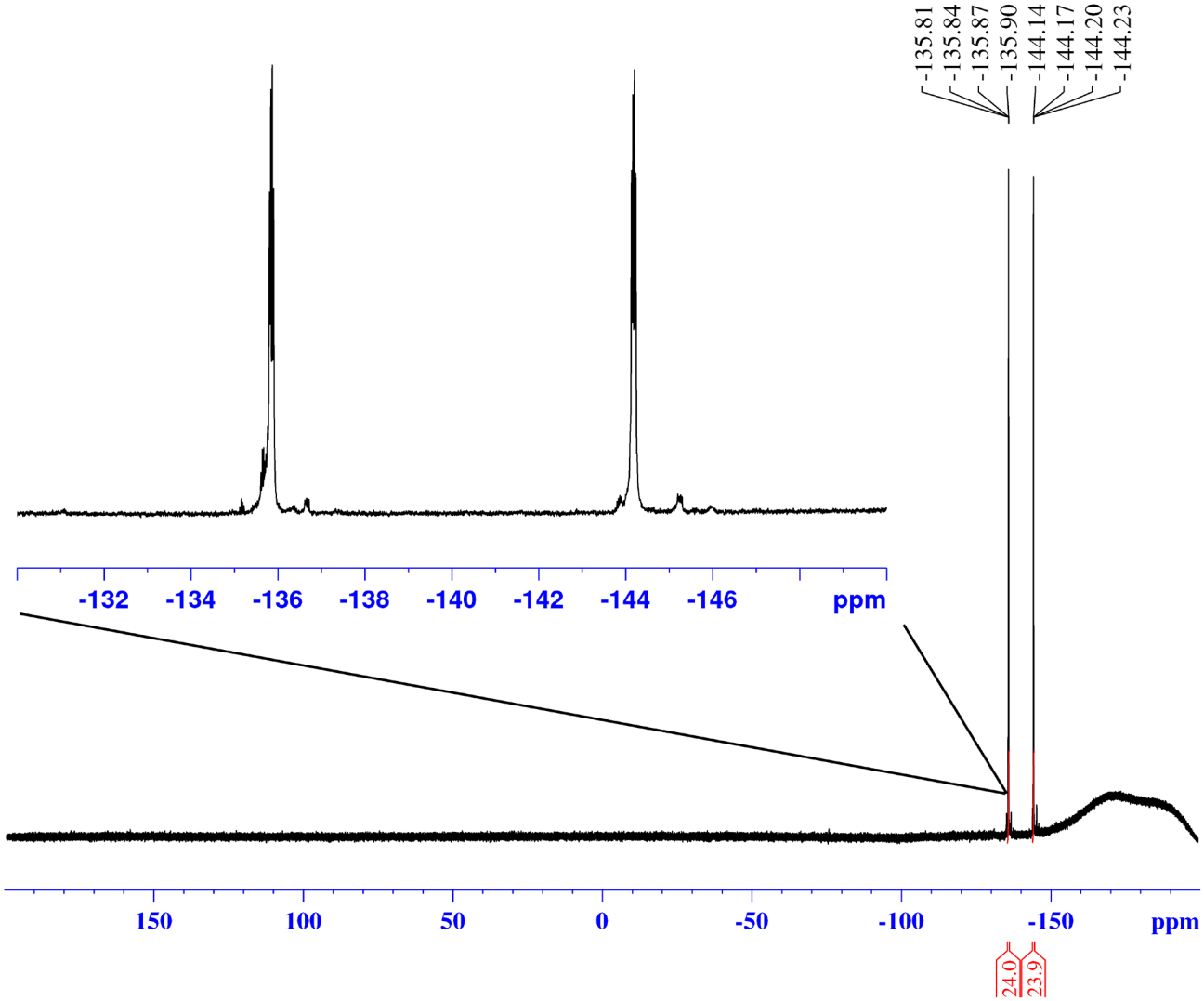
======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

BRUKER

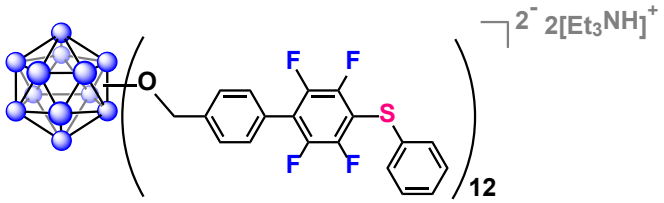


Current Data Parameters
NAME Jan22-2016
EXPNO 72
PROCNO 1

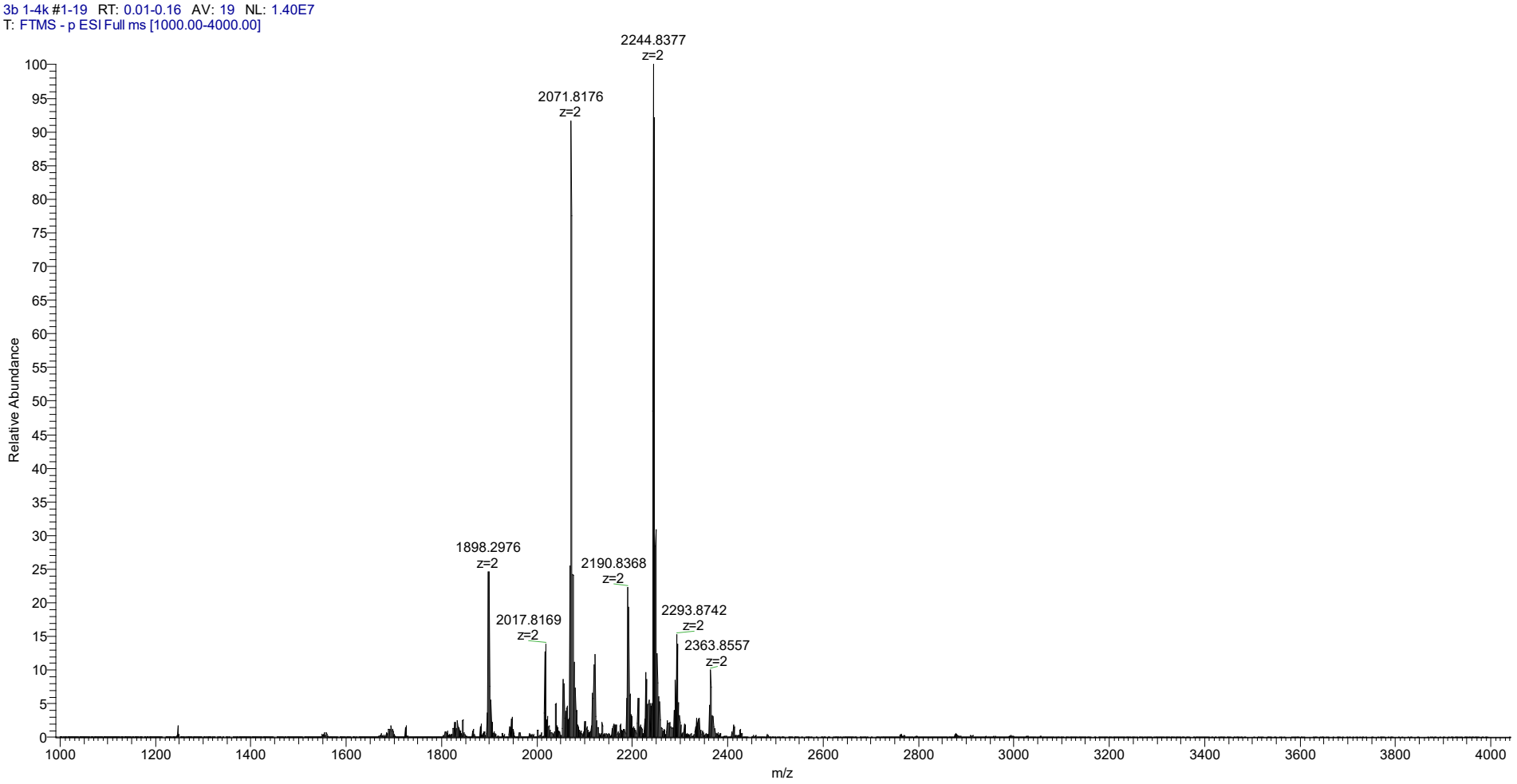
F2 - Acquisition Parameters
Date_ 20160122
Time 15.17
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

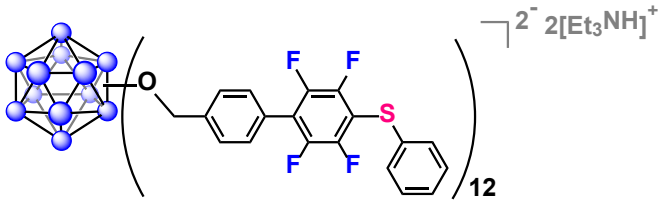
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

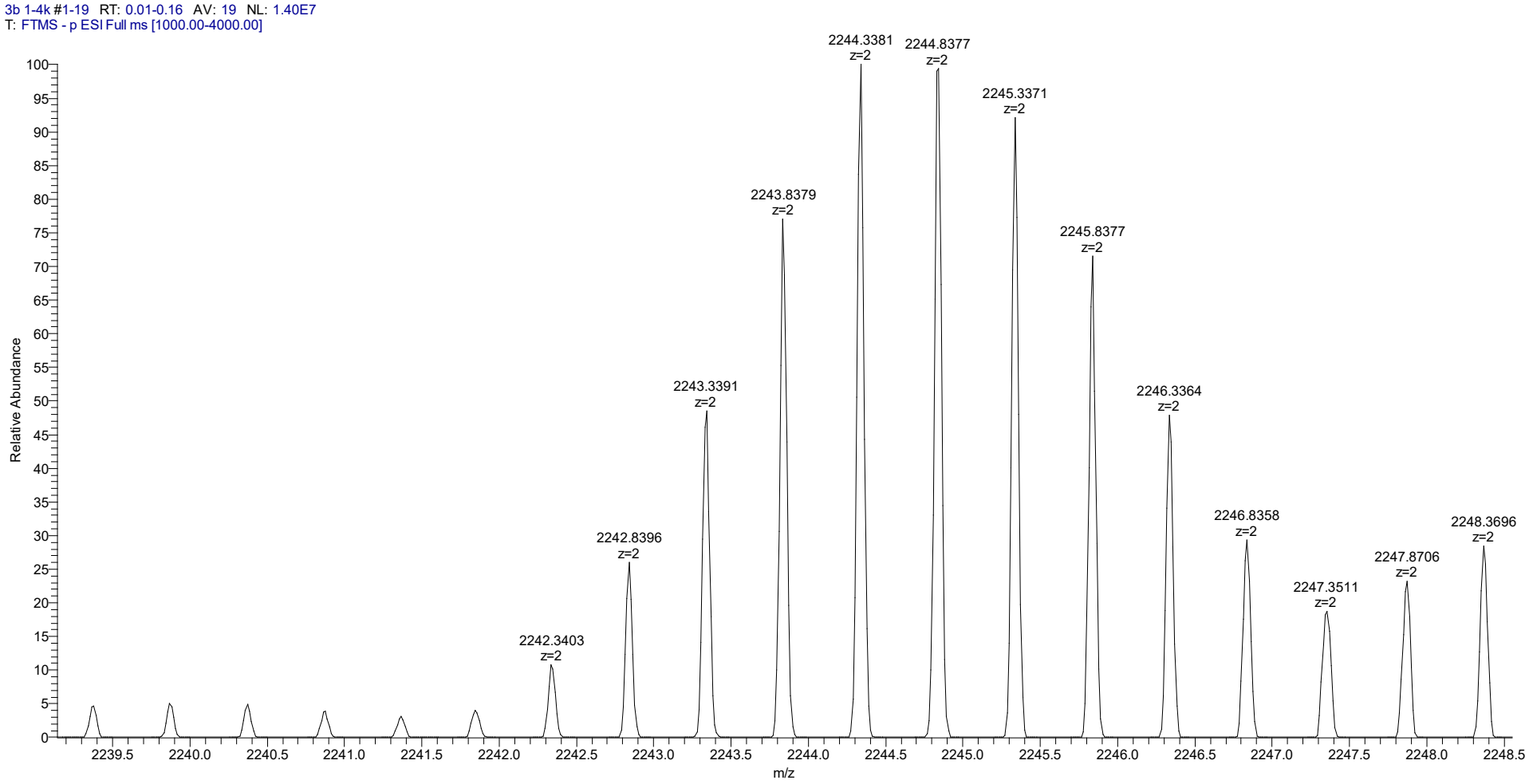


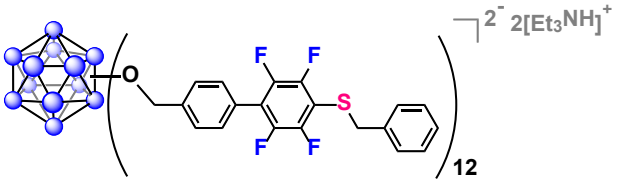
Q Exactive
High-Res Mass Spec



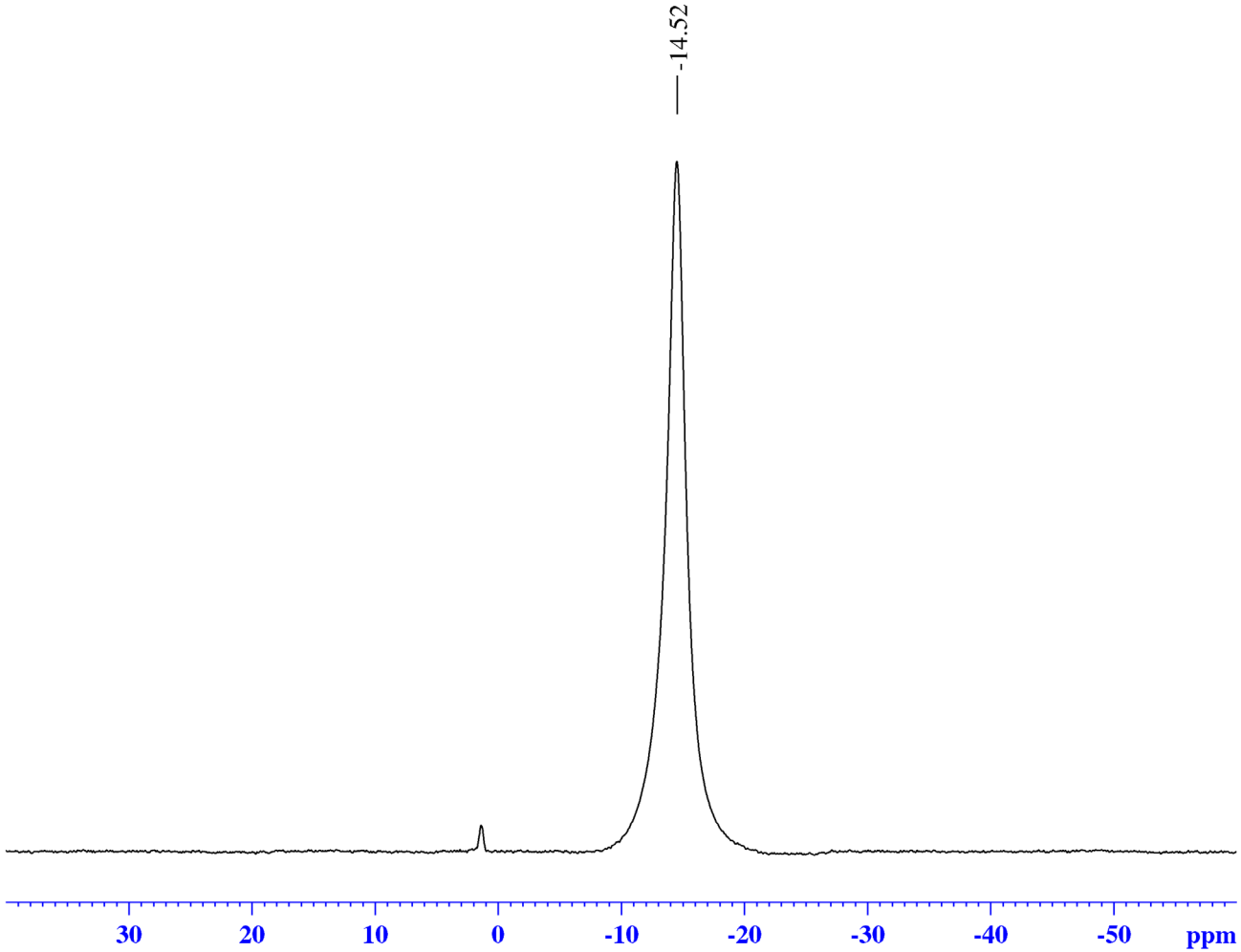


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

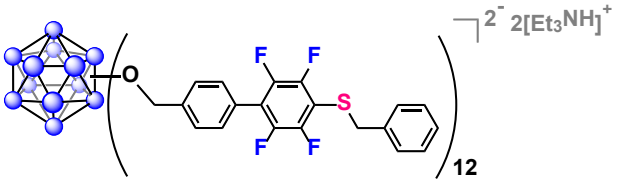


Current Data Parameters
NAME 0120
EXPNO 71
PROCNO 1

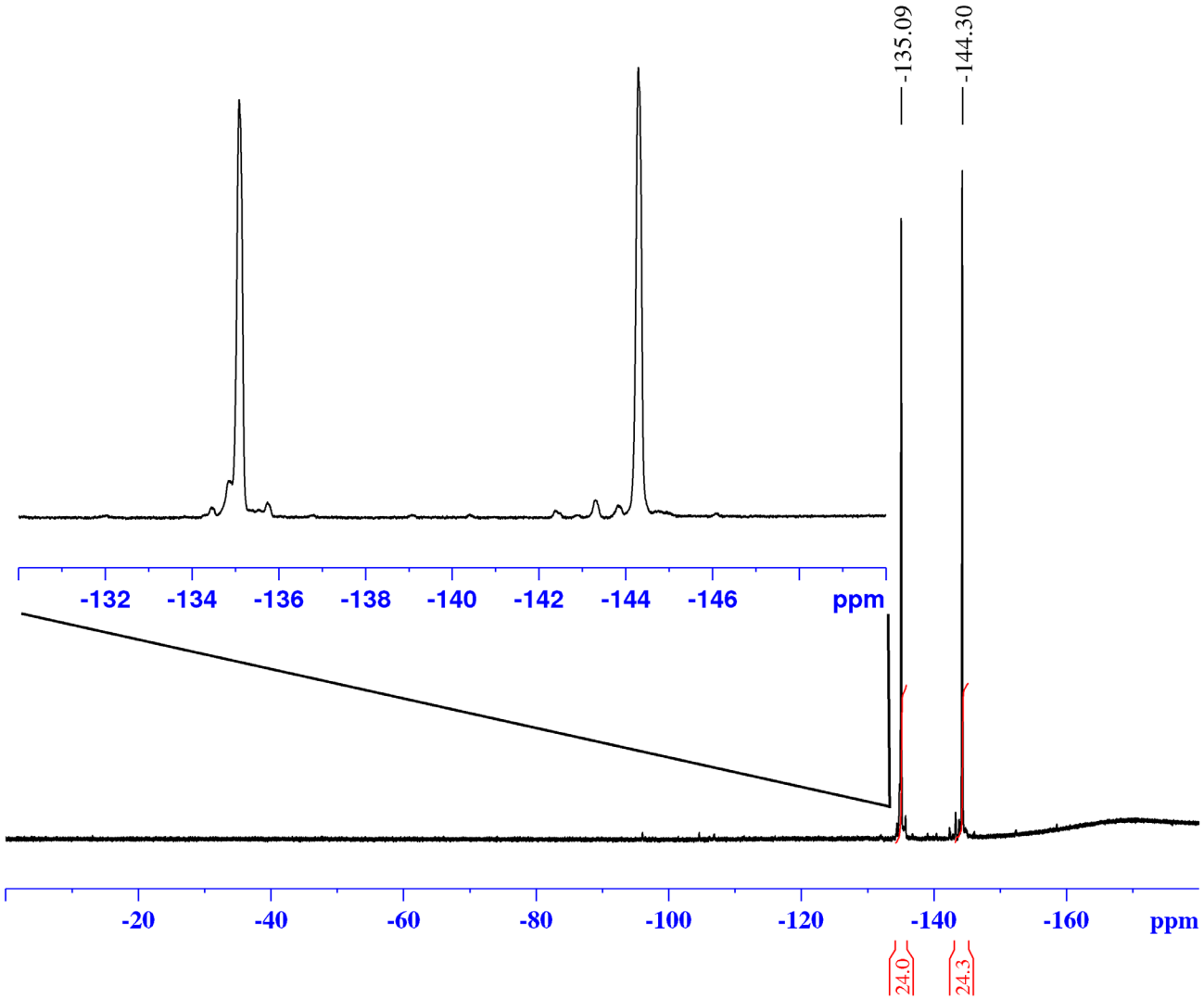
F2 - Acquisition Parameters
Date_ 20160120
Time 18.53
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

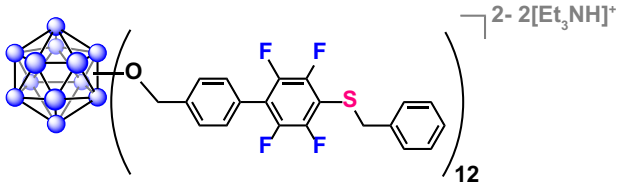


Current Data Parameters
NAME 0120
EXPNO 70
PROCNO 1

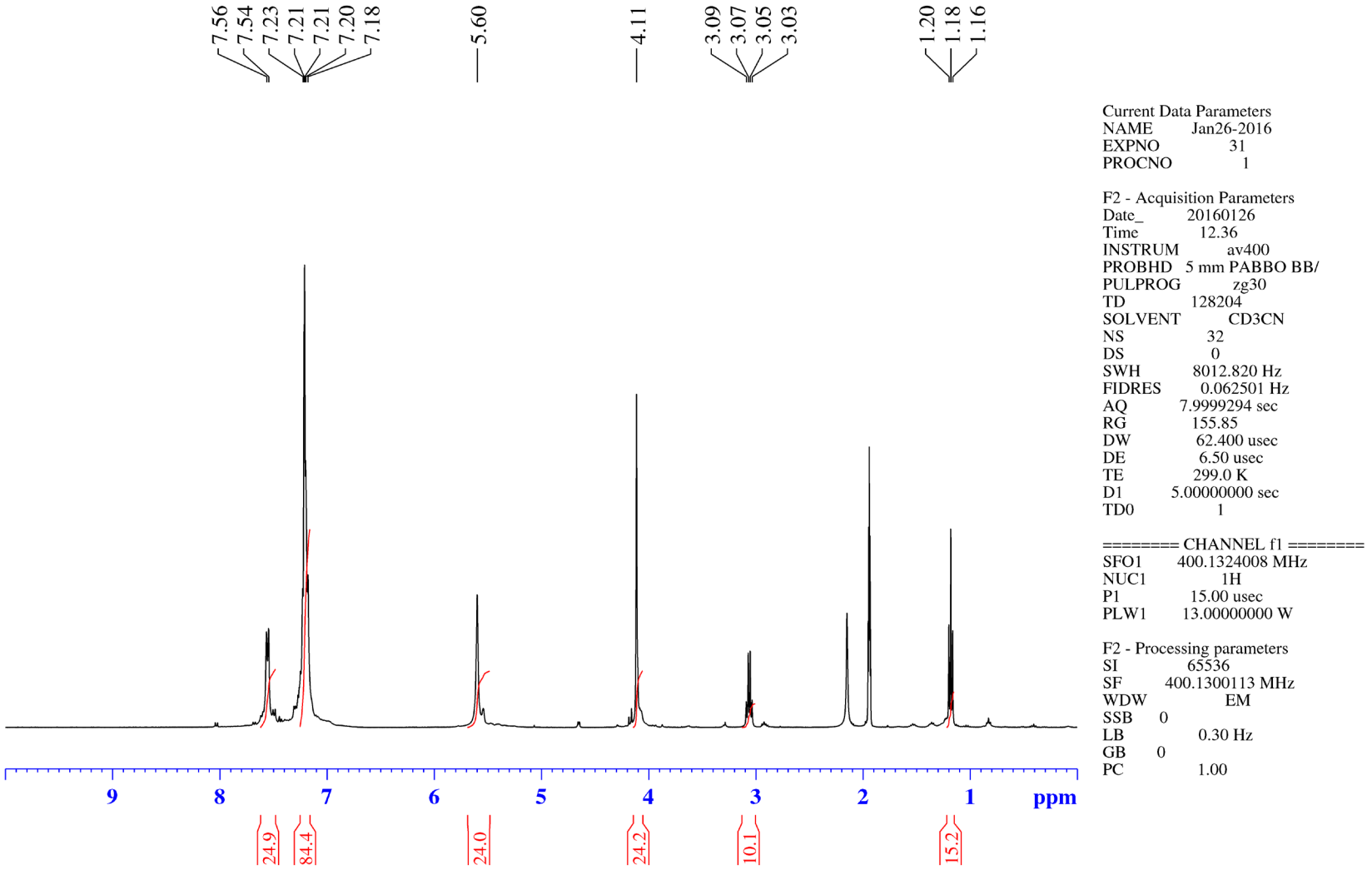
F2 - Acquisition Parameters
Date_ 20160120
Time 18.50
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

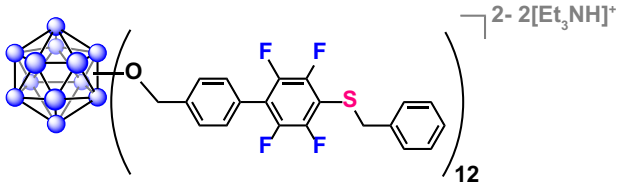


Current Data Parameters
NAME Jan26-2016
EXPNO 31
PROCNO 1

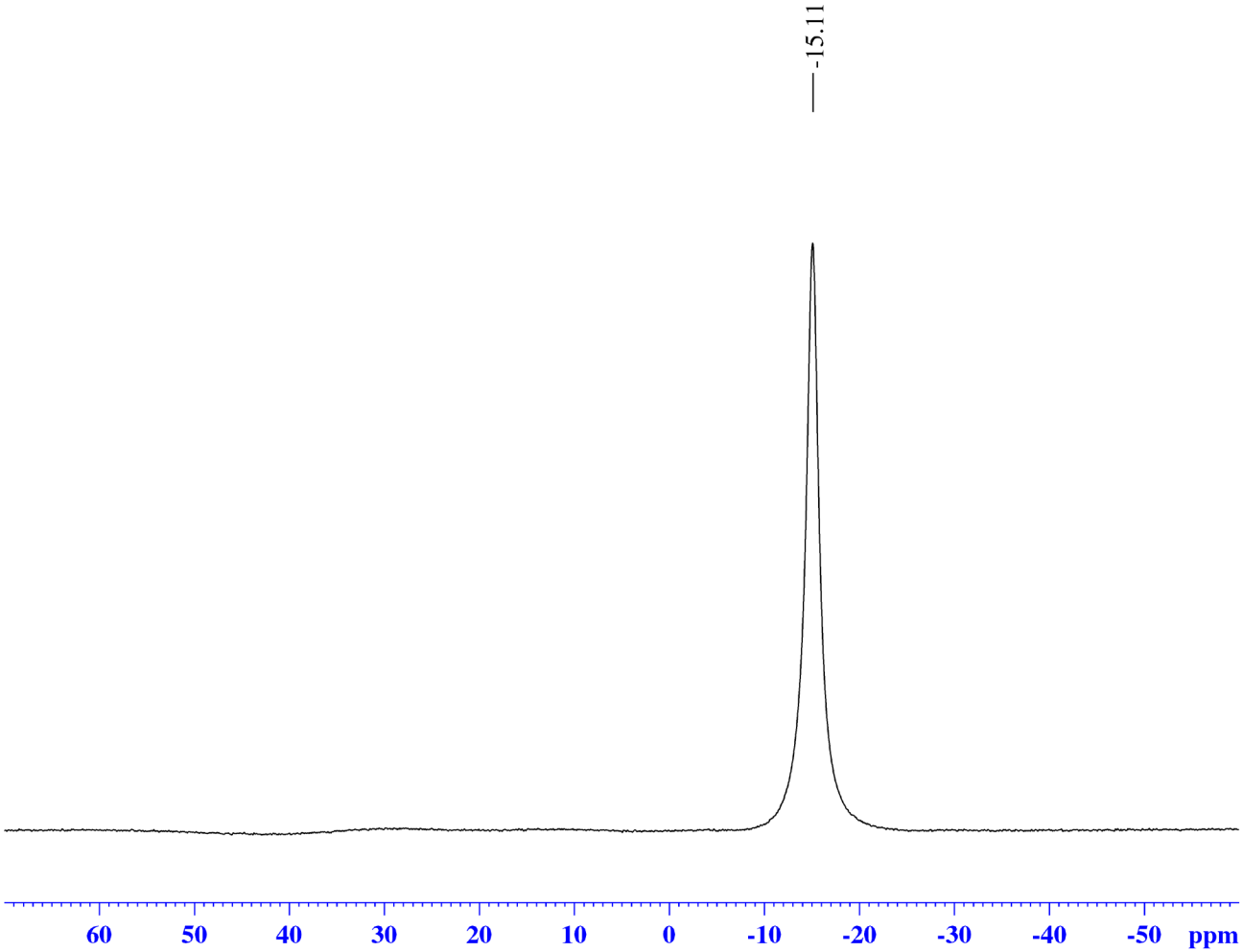
F2 - Acquisition Parameters
Date_ 20160126
Time 12.36
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 128204
SOLVENT CD3CN
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.062501 Hz
AQ 7.9999294 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B {^{1}H} NMR



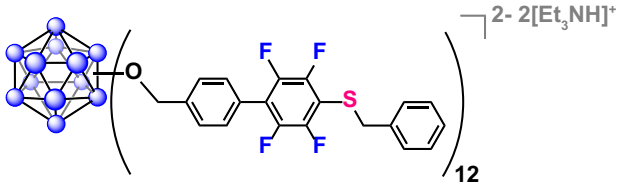
Current Data Parameters
NAME Jan26-2016
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160126
Time 12.28
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgdc.js
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
D11 0.03000000 sec
TD0 1

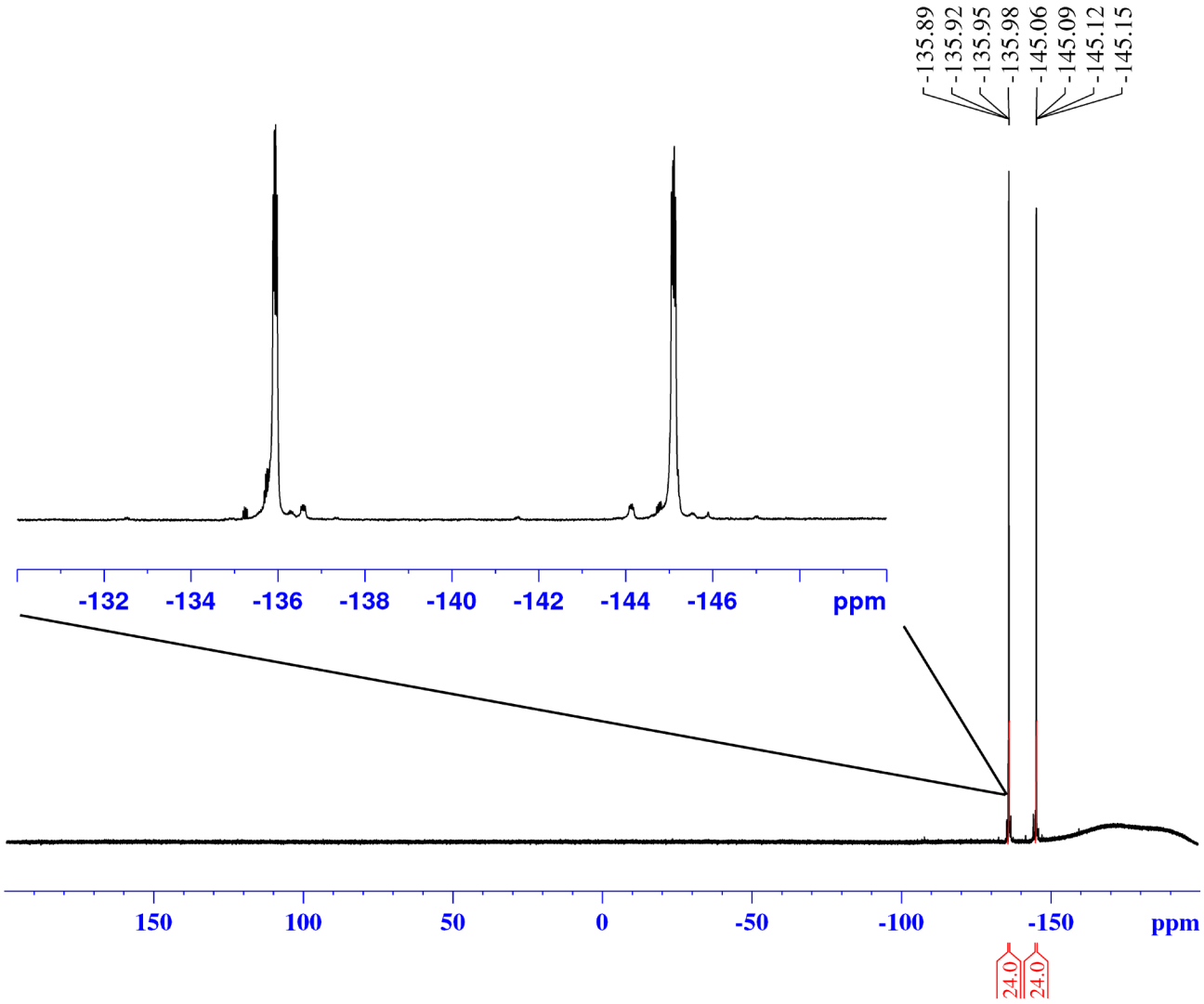
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

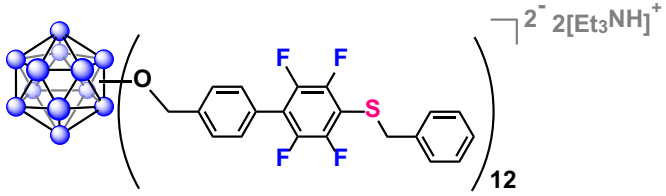


Current Data Parameters
NAME Jan26-2016
EXPNO 32
PROCNO 1

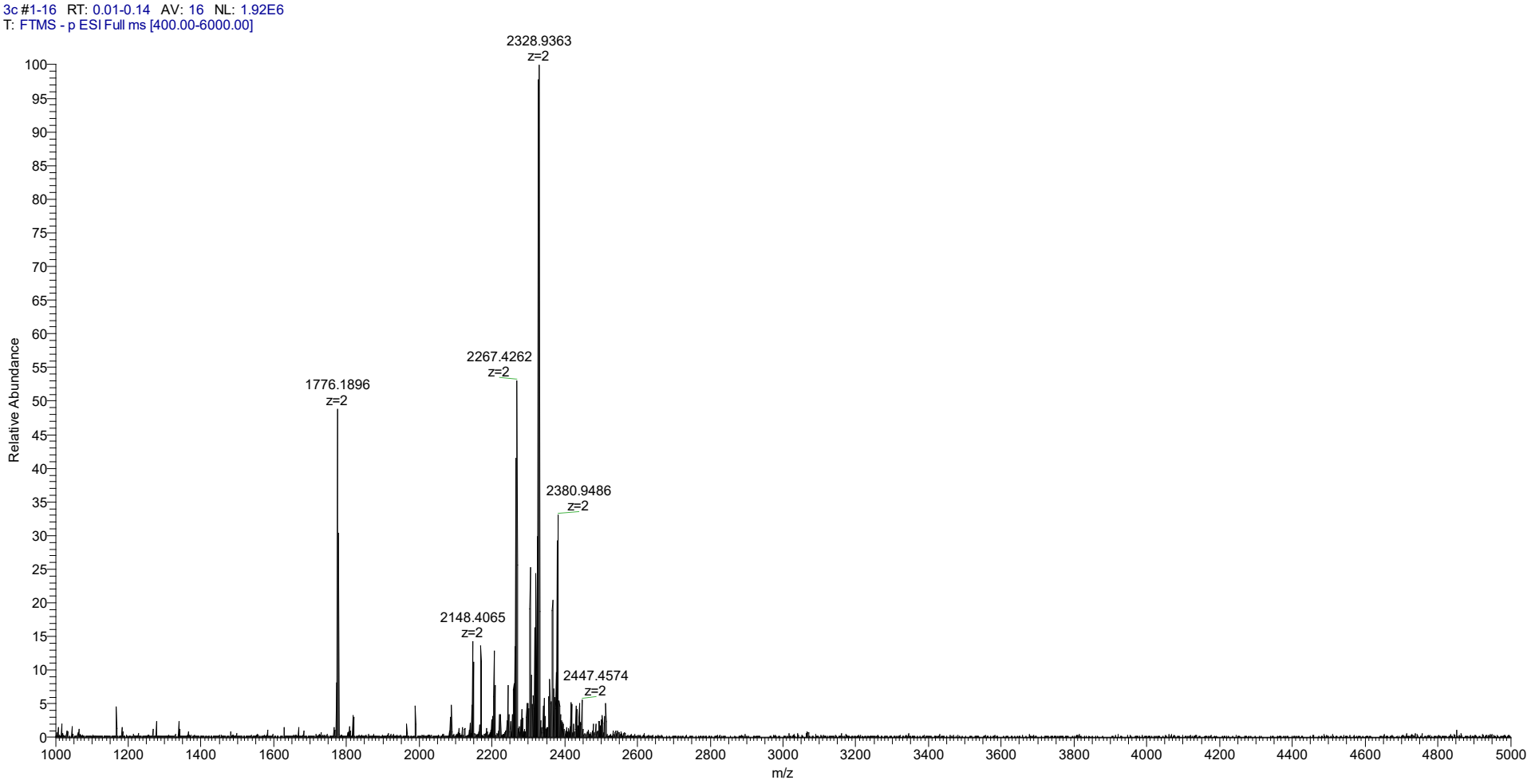
F2 - Acquisition Parameters
Date_ 20160126
Time 12.40
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

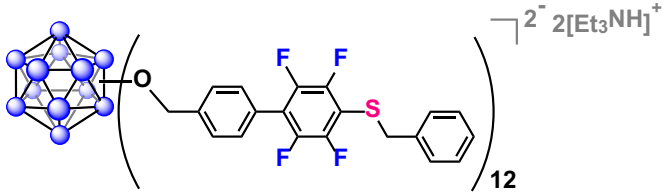
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



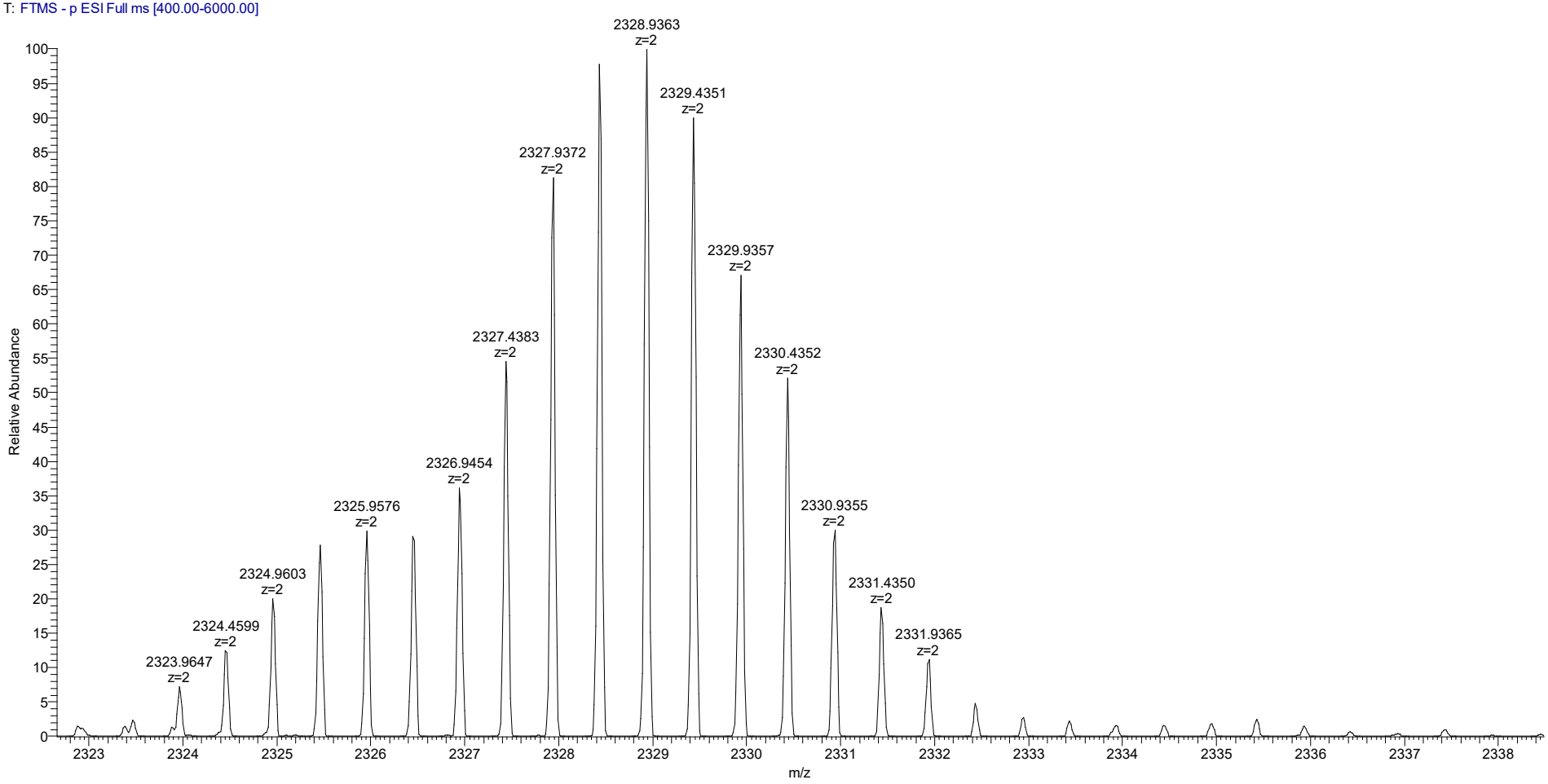
Q Exactive
High-Res Mass Spec

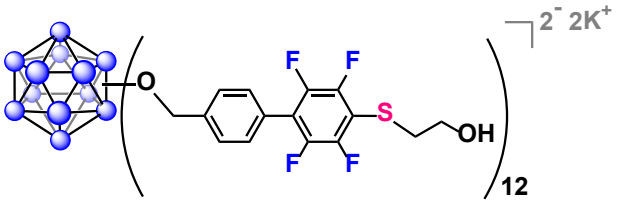




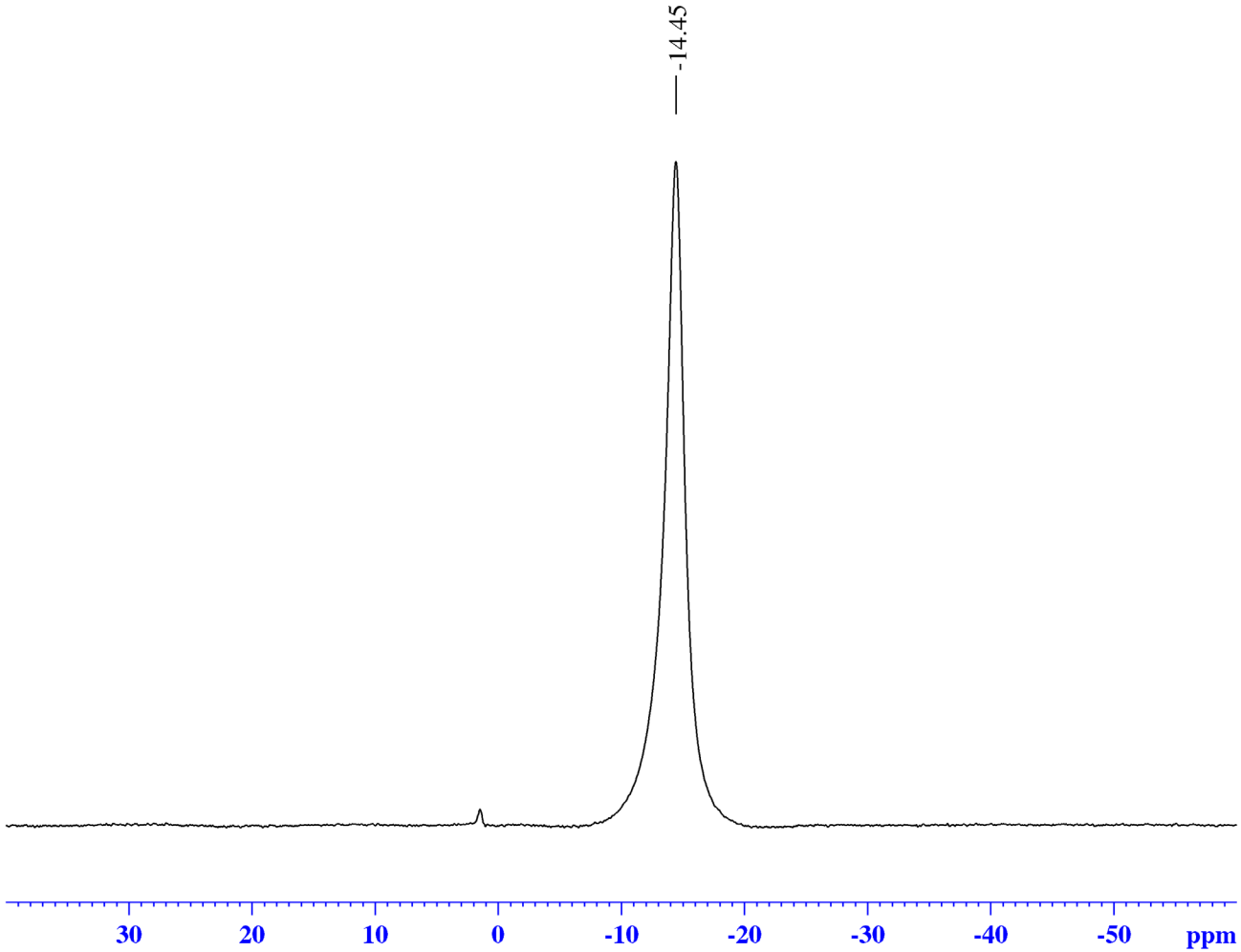
Q Exactive
High-Res Mass Spec

3c #1-16 RT: 0.01-0.14 AV: 16 NL: 1.92E6
T: FTMS - p ESI Full ms [400.00-6000.00]





in situ ^{11}B NMR

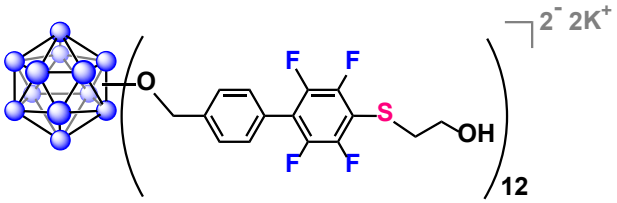


Current Data Parameters
NAME 0110
EXPNO 41
PROCNO 1

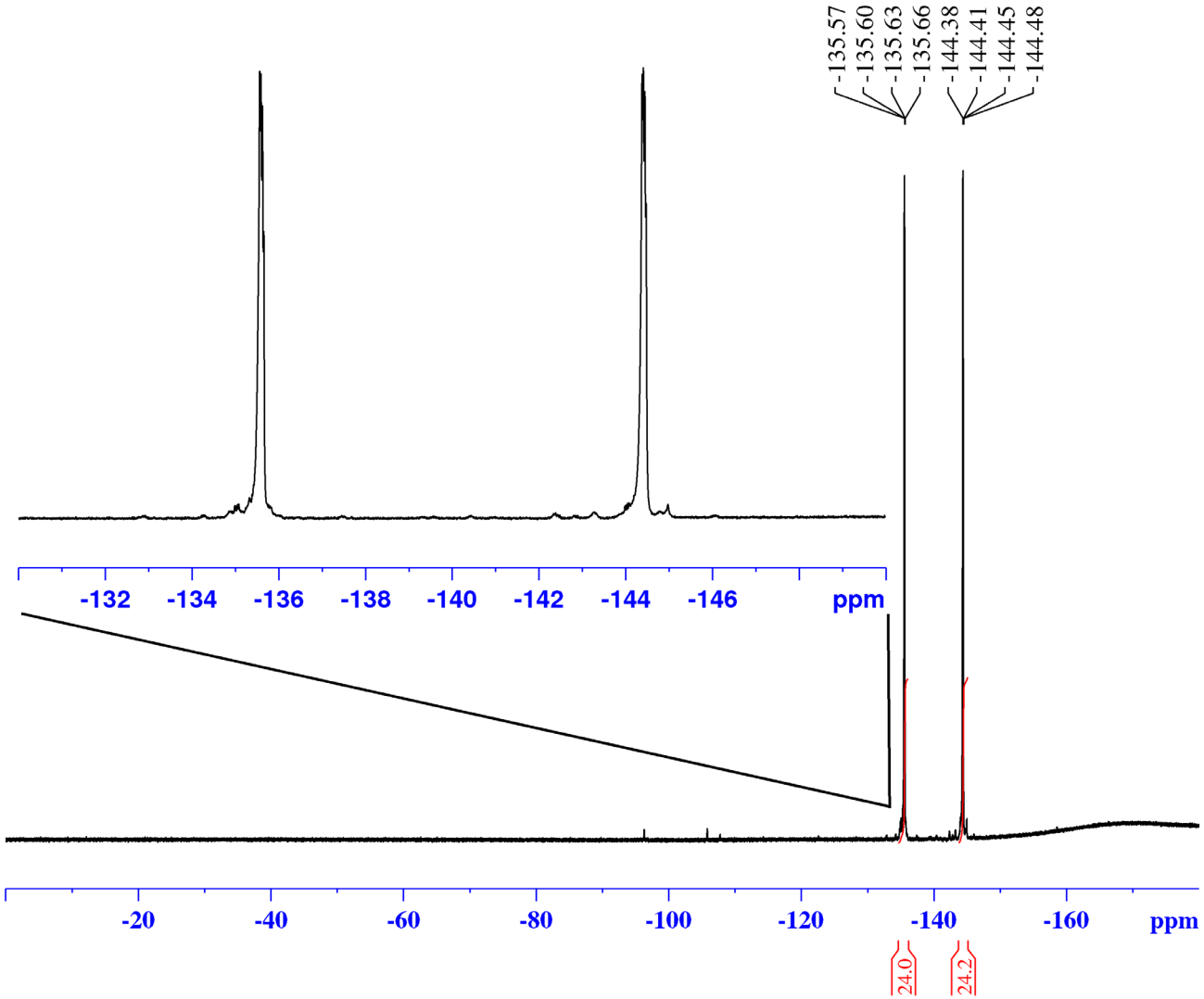
F2 - Acquisition Parameters
Date_ 20160110
Time 20.38
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

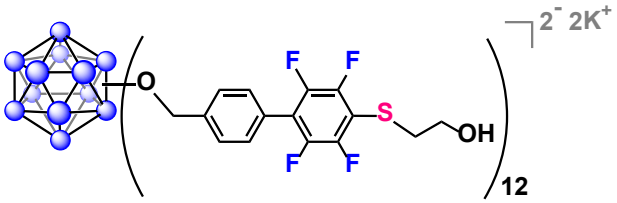


Current Data Parameters
NAME 0110
EXPNO 40
PROCNO 1

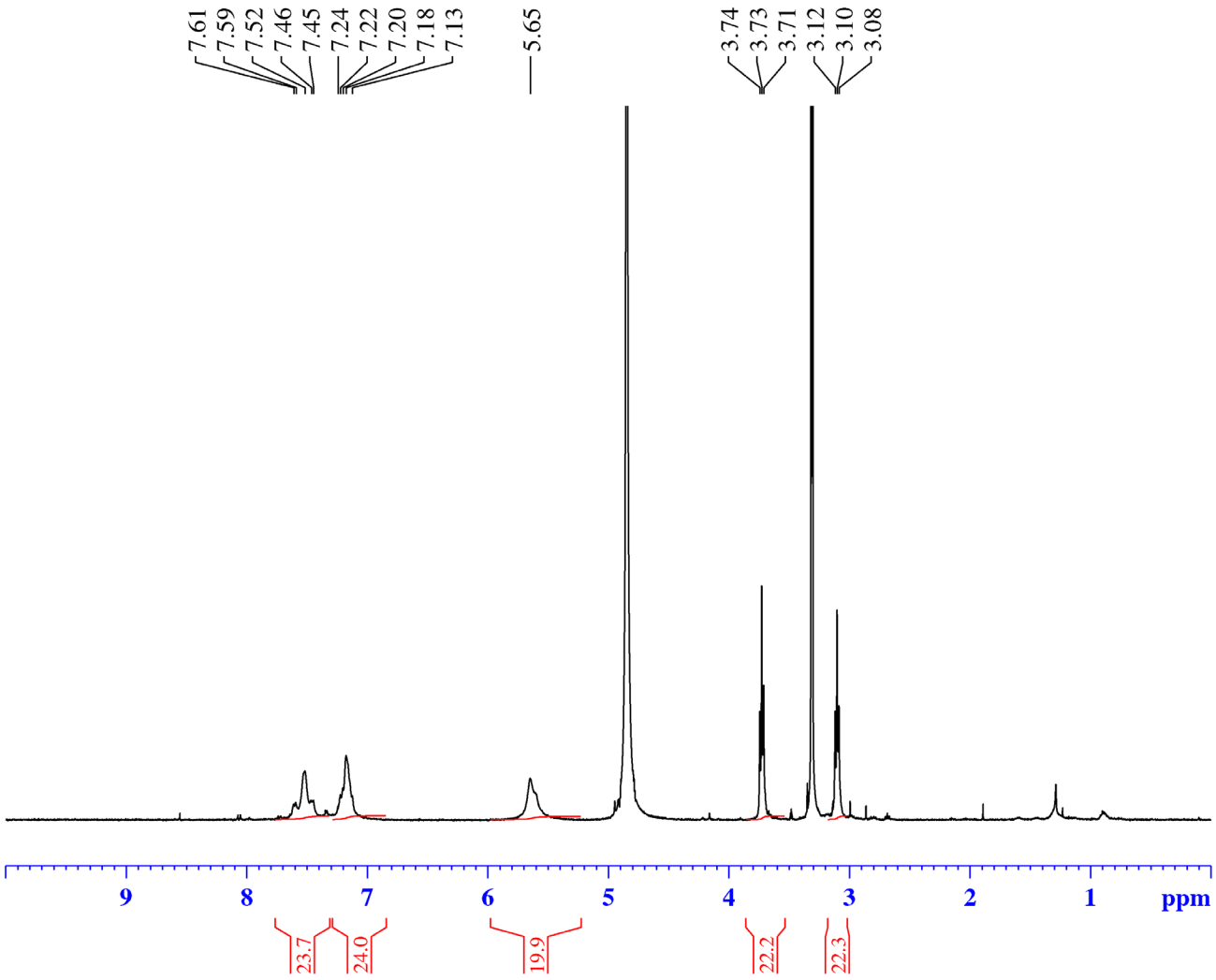
F2 - Acquisition Parameters
Date_ 20160110
Time 20.34
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

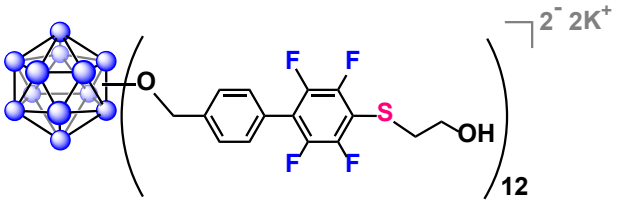


Current Data Parameters
NAME G2 2ME 0111 0110 (MeOD)
EXPNO 1160
PROCNO 1

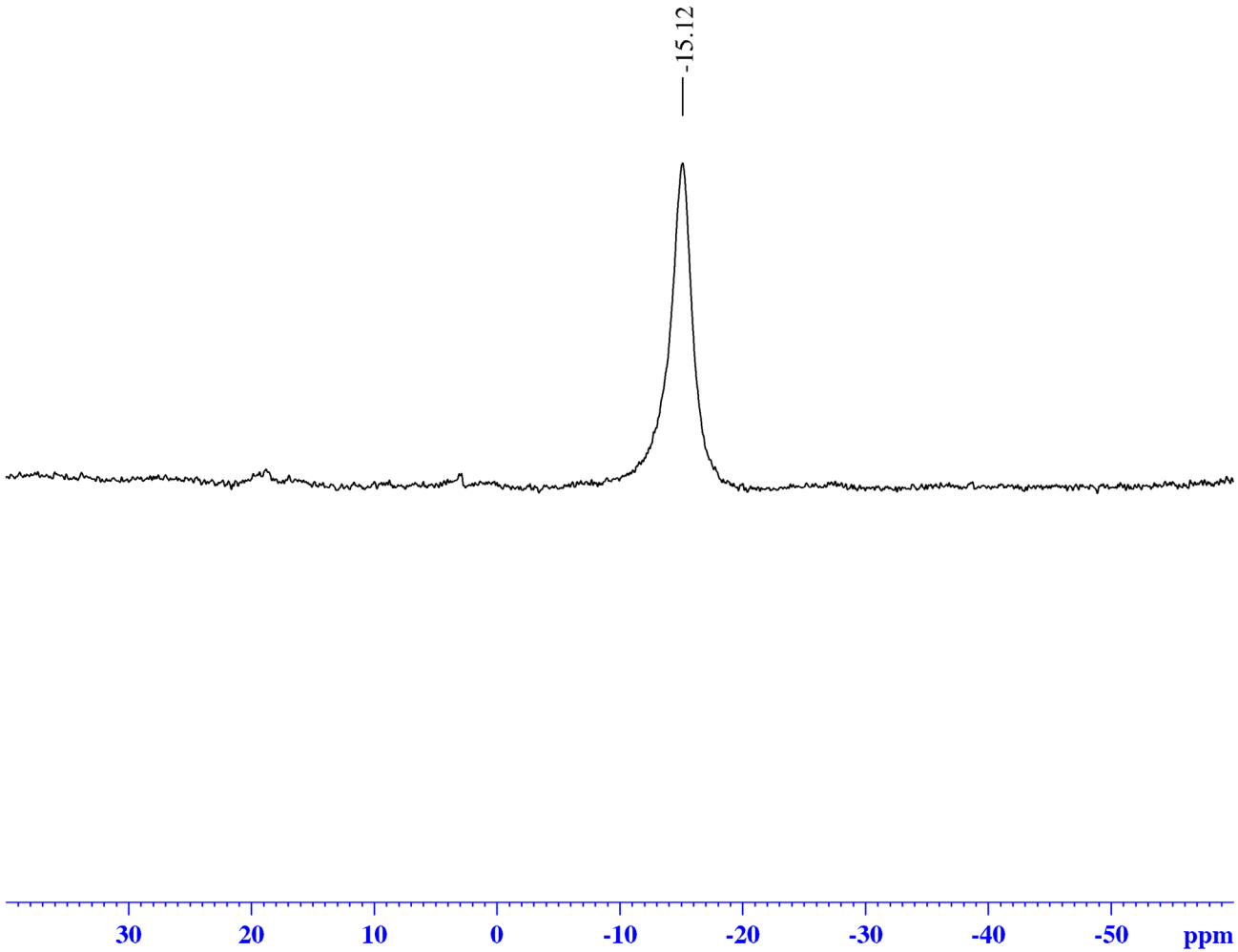
F2 - Acquisition Parameters
Date_ 20160112
Time 16.27
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

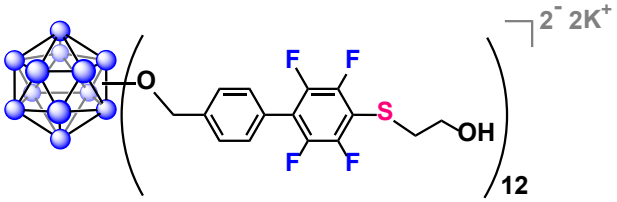


Current Data Parameters
NAME G2 2ME 0111 0110 (MeOD)
EXPNO 1162
PROCNO 1

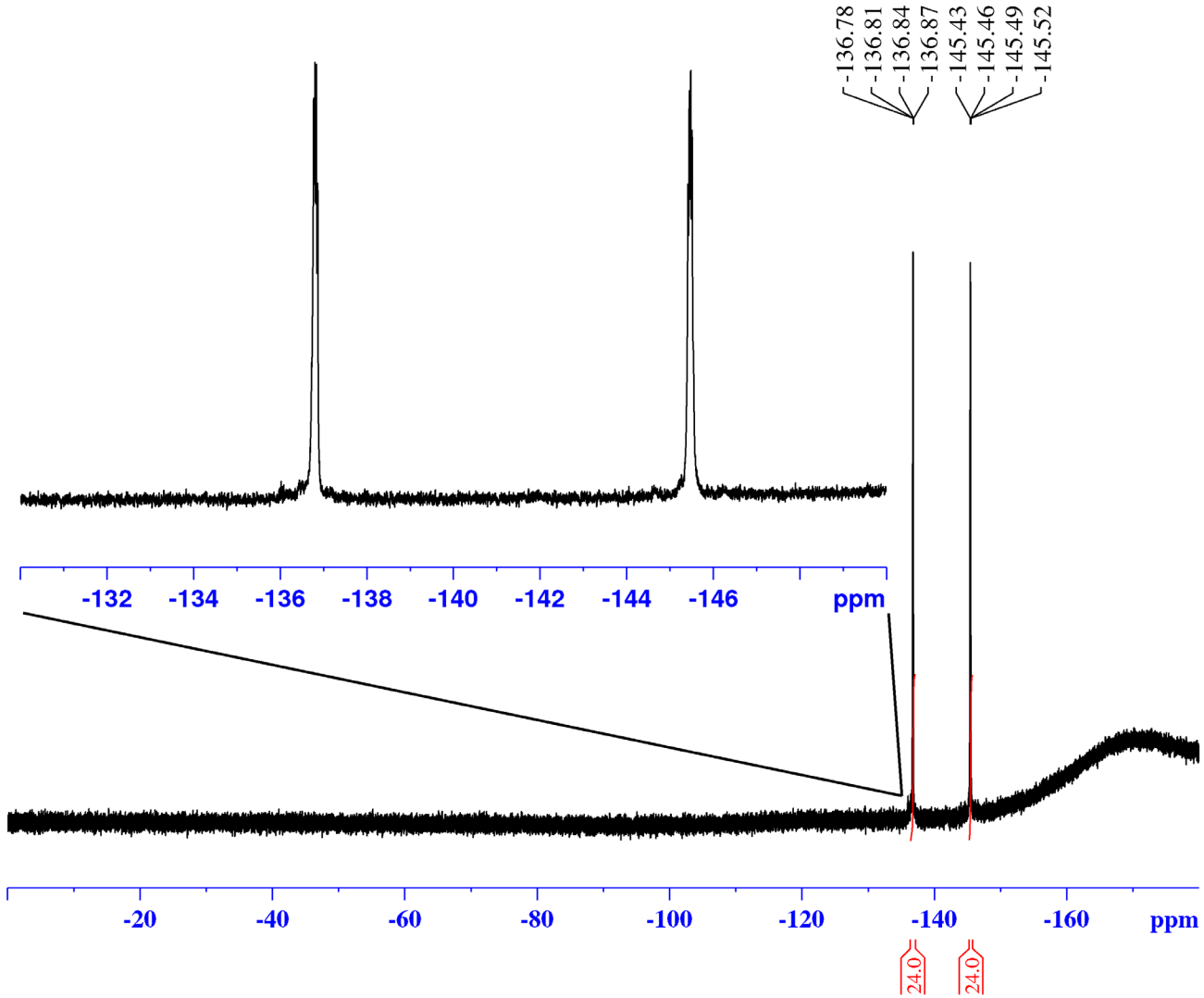
F2 - Acquisition Parameters
Date_ 20160112
Time 16.35
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

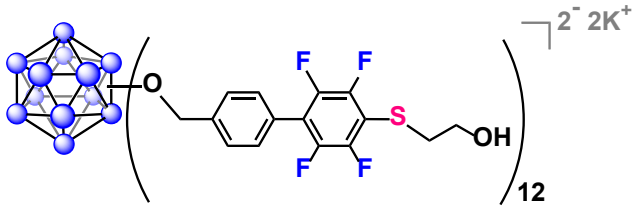


Current Data Parameters
NAME G2 2ME 0111 0110 (MeOD)
EXPNO 1161
PROCNO 1

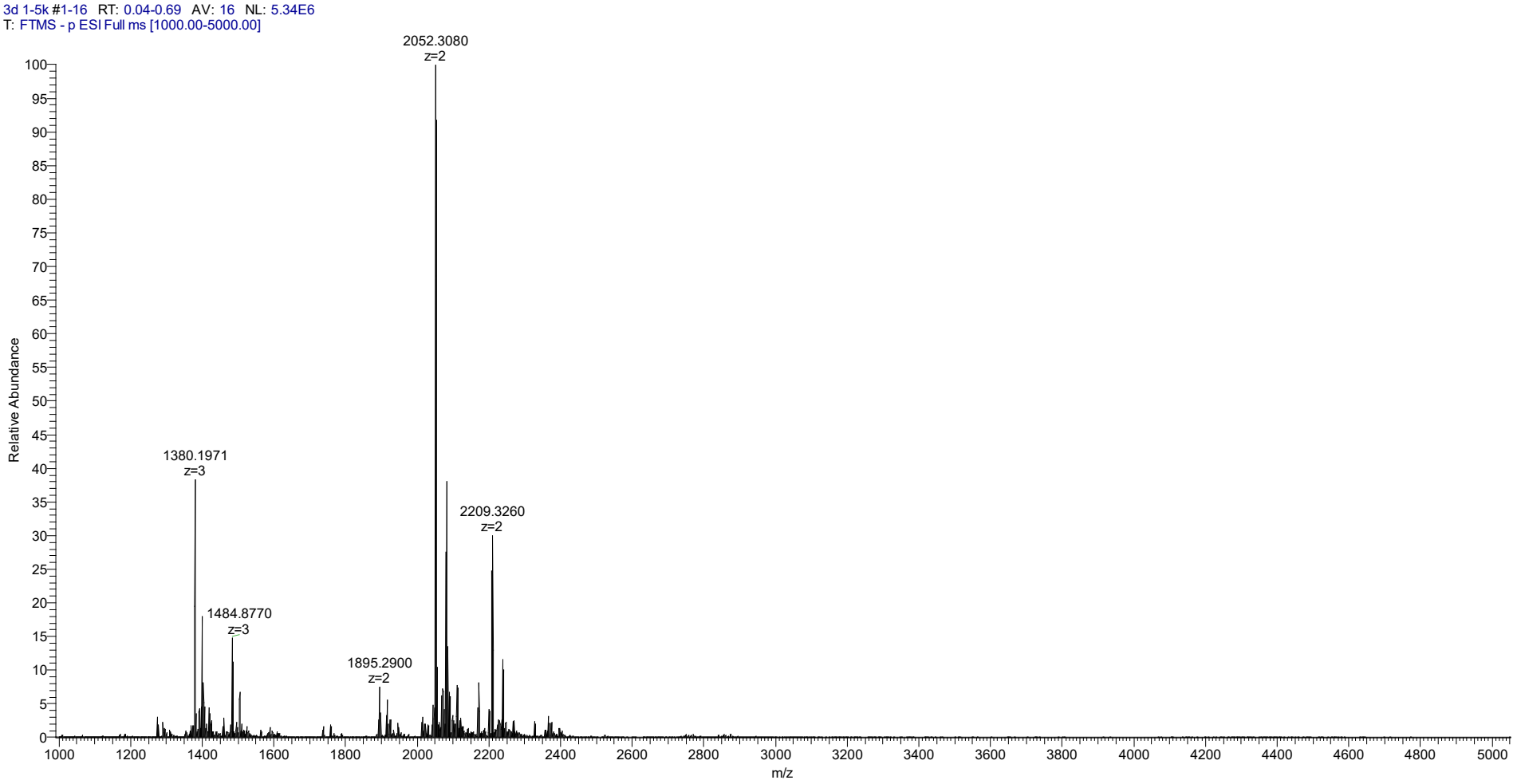
F2 - Acquisition Parameters
Date_ 20160112
Time 16.32
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

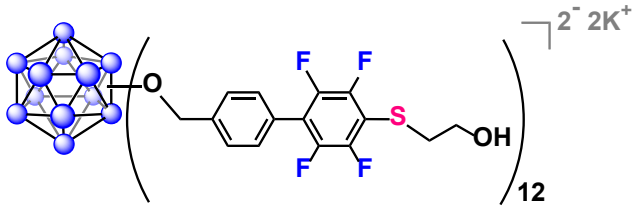
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

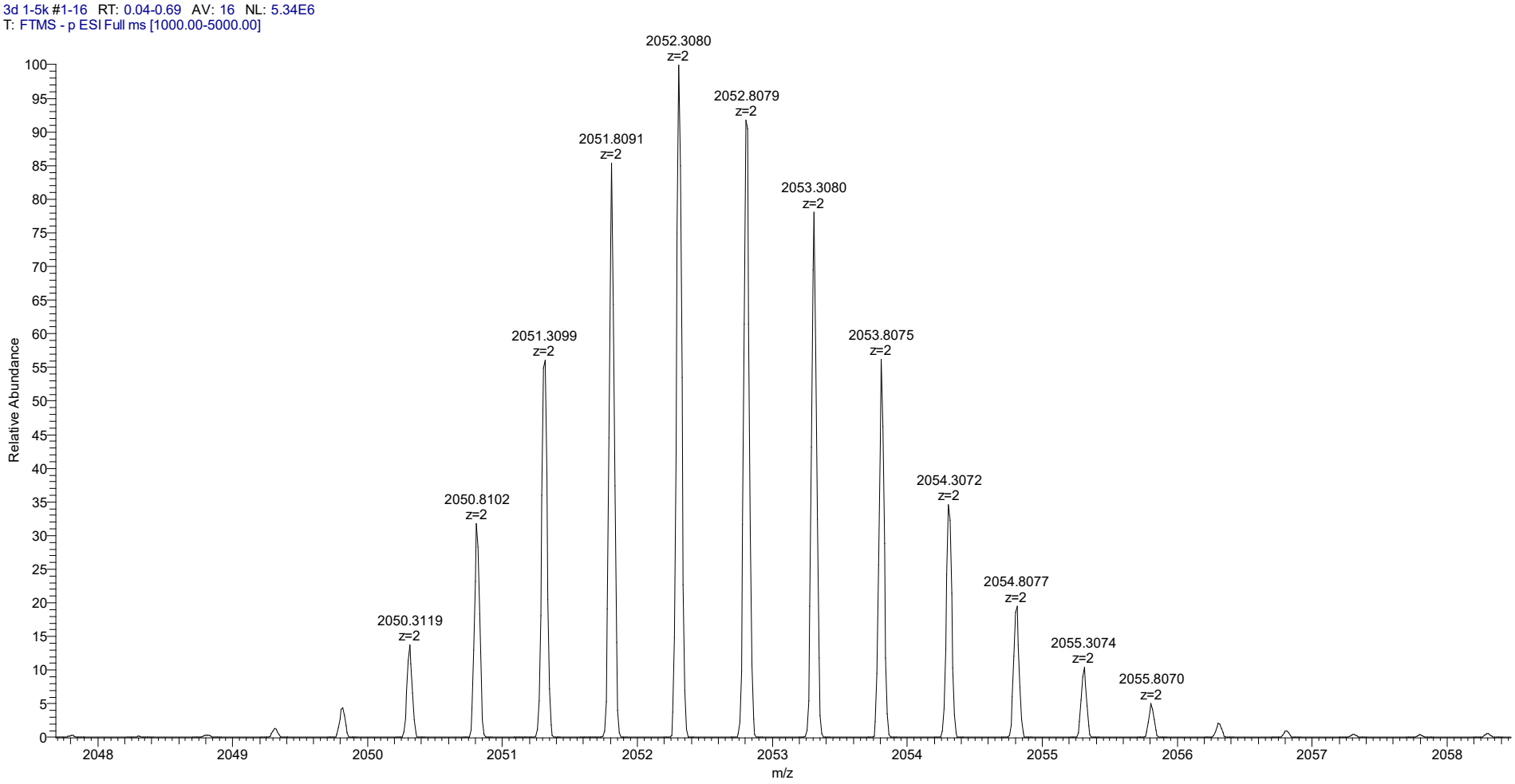


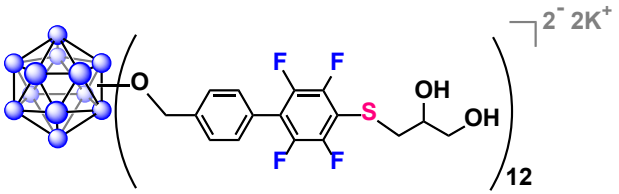
Q Exactive
High-Res Mass Spec



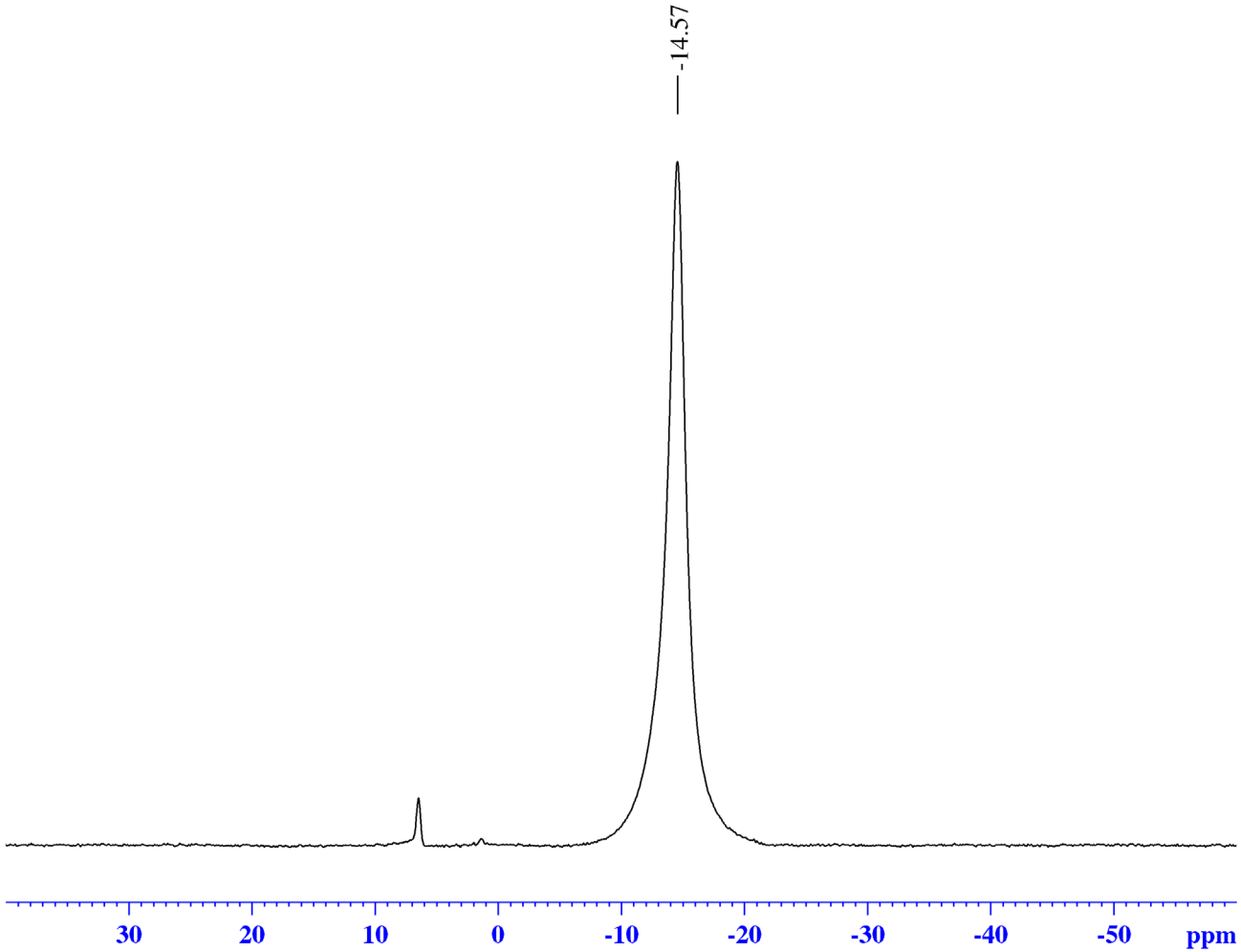


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

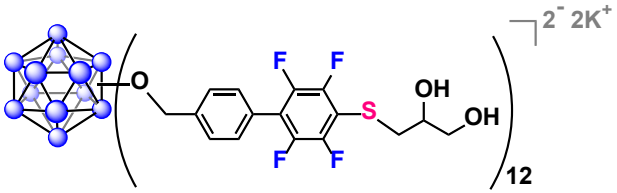


Current Data Parameters
NAME 0110
EXPNO 61
PROCNO 1

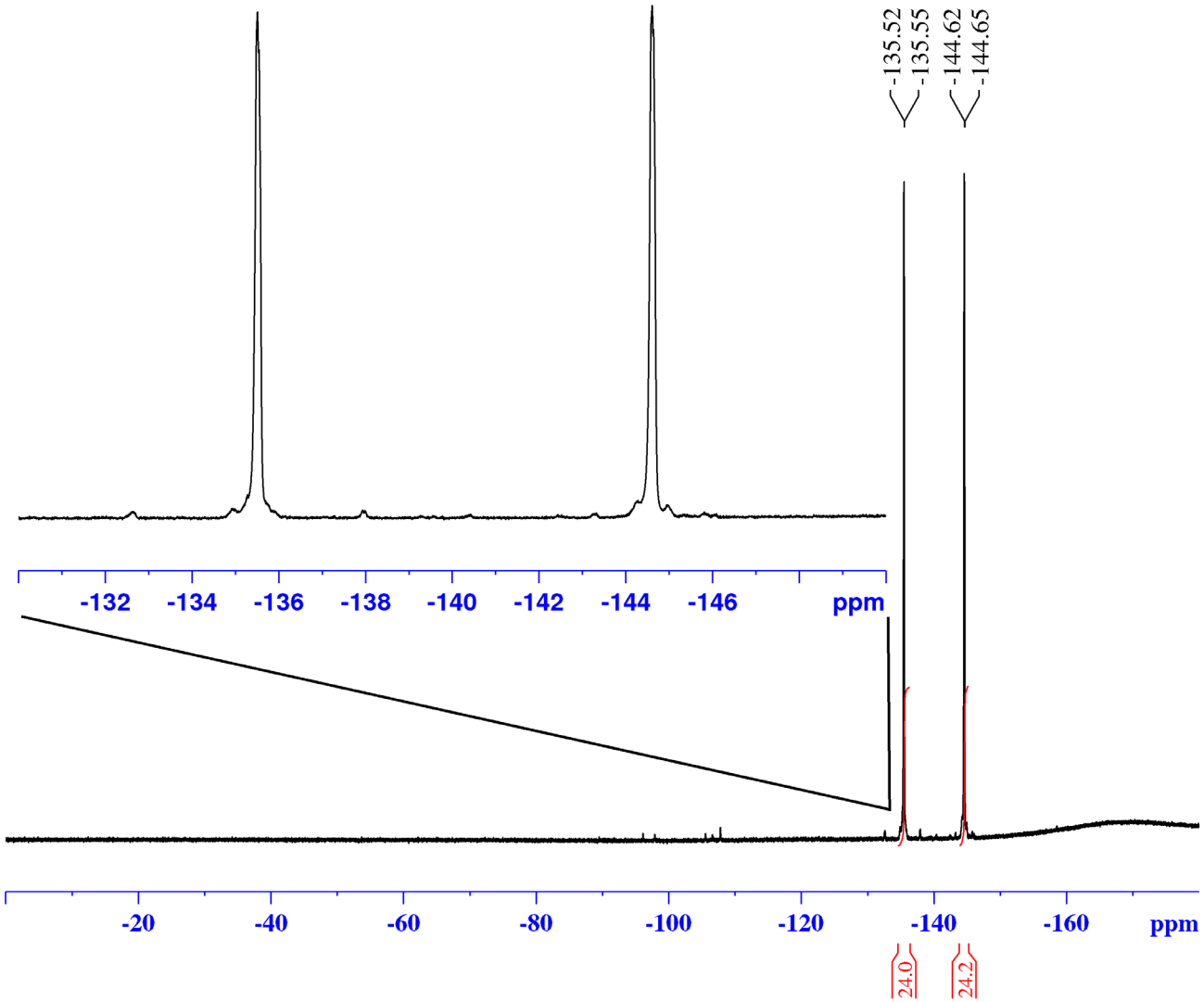
F2 - Acquisition Parameters
Date_ 20160110
Time 20.56
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

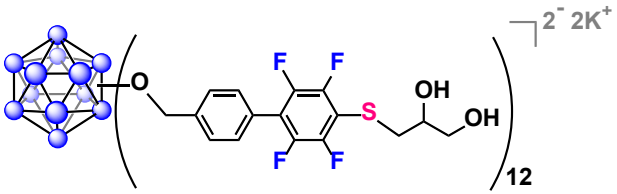


Current Data Parameters
NAME 0110
EXPNO 60
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160110
Time 20.53
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

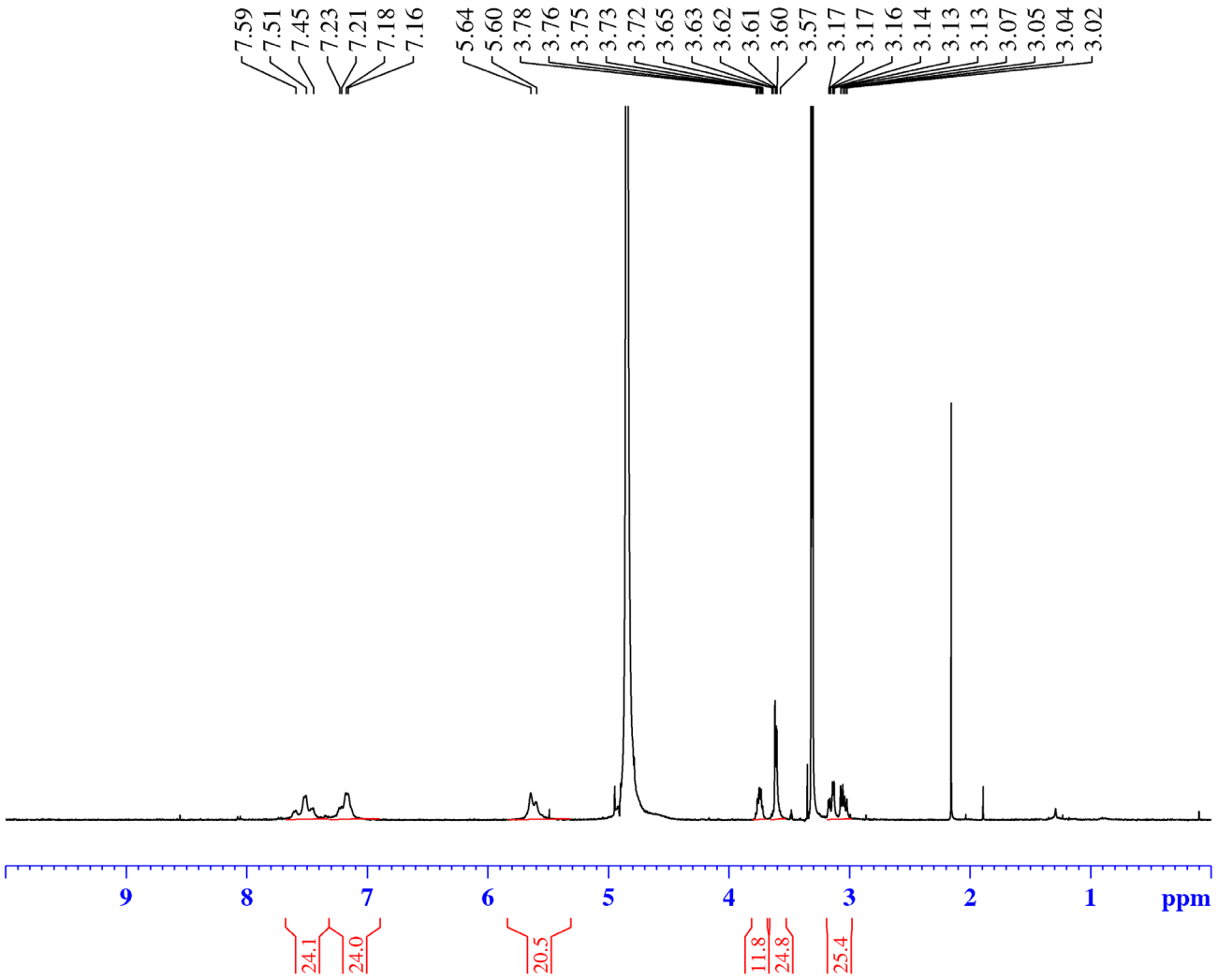
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

BRUKER

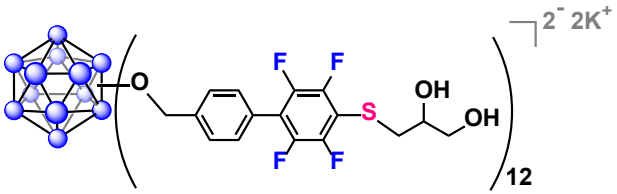


Current Data Parameters
NAME G2 Glycerol 0111 0110 (MeOD)
EXPNO 250
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160112
Time 22.11
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

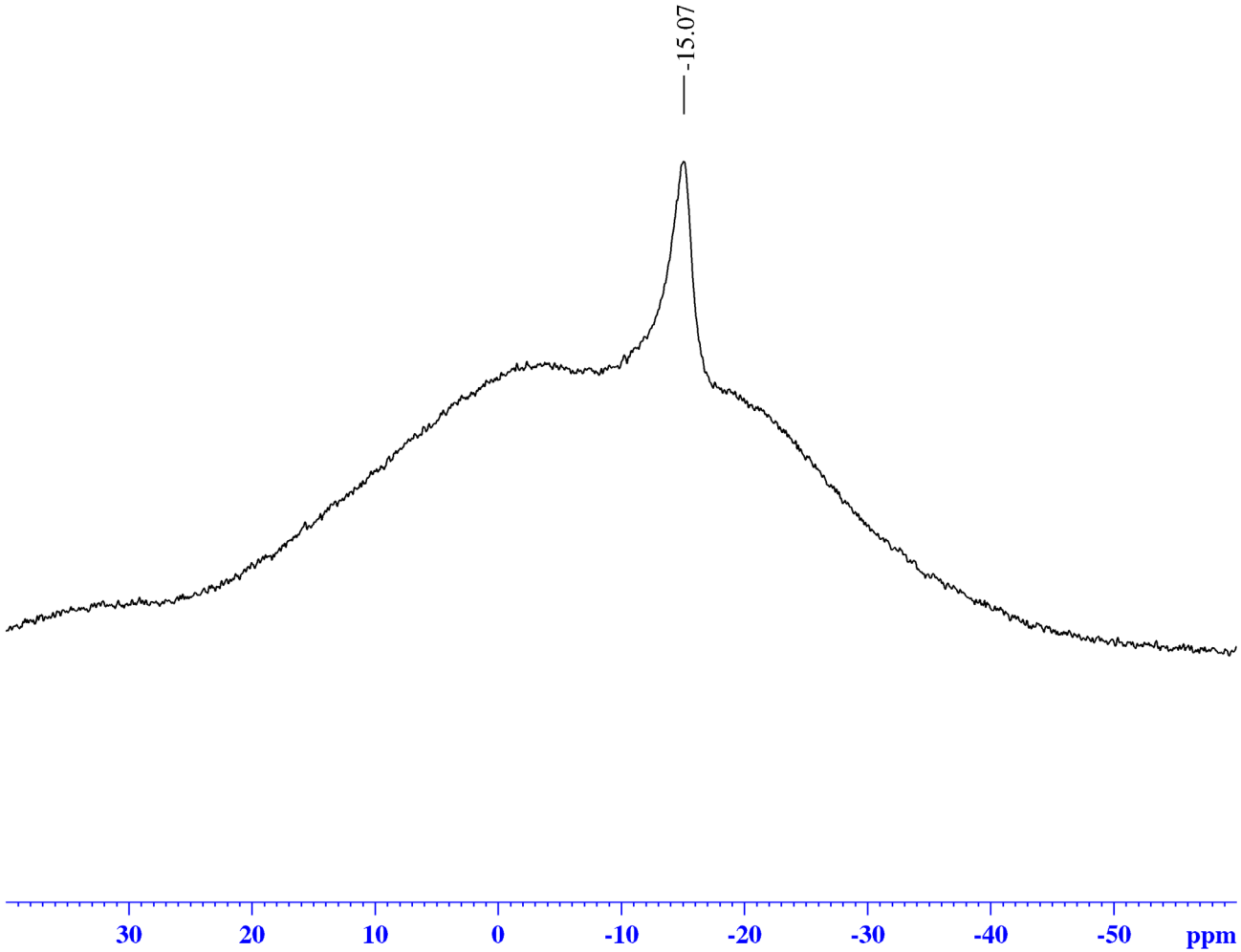
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

BRUKER

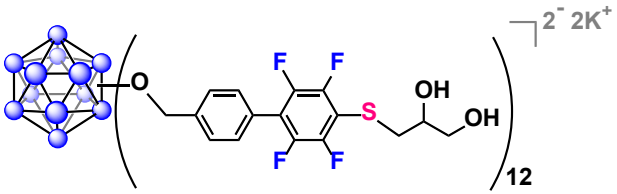


Current Data Parameters
NAME G2 Glycerol 0111 0110 (MeOD)
EXPNO 252
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160112
Time 22.18
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

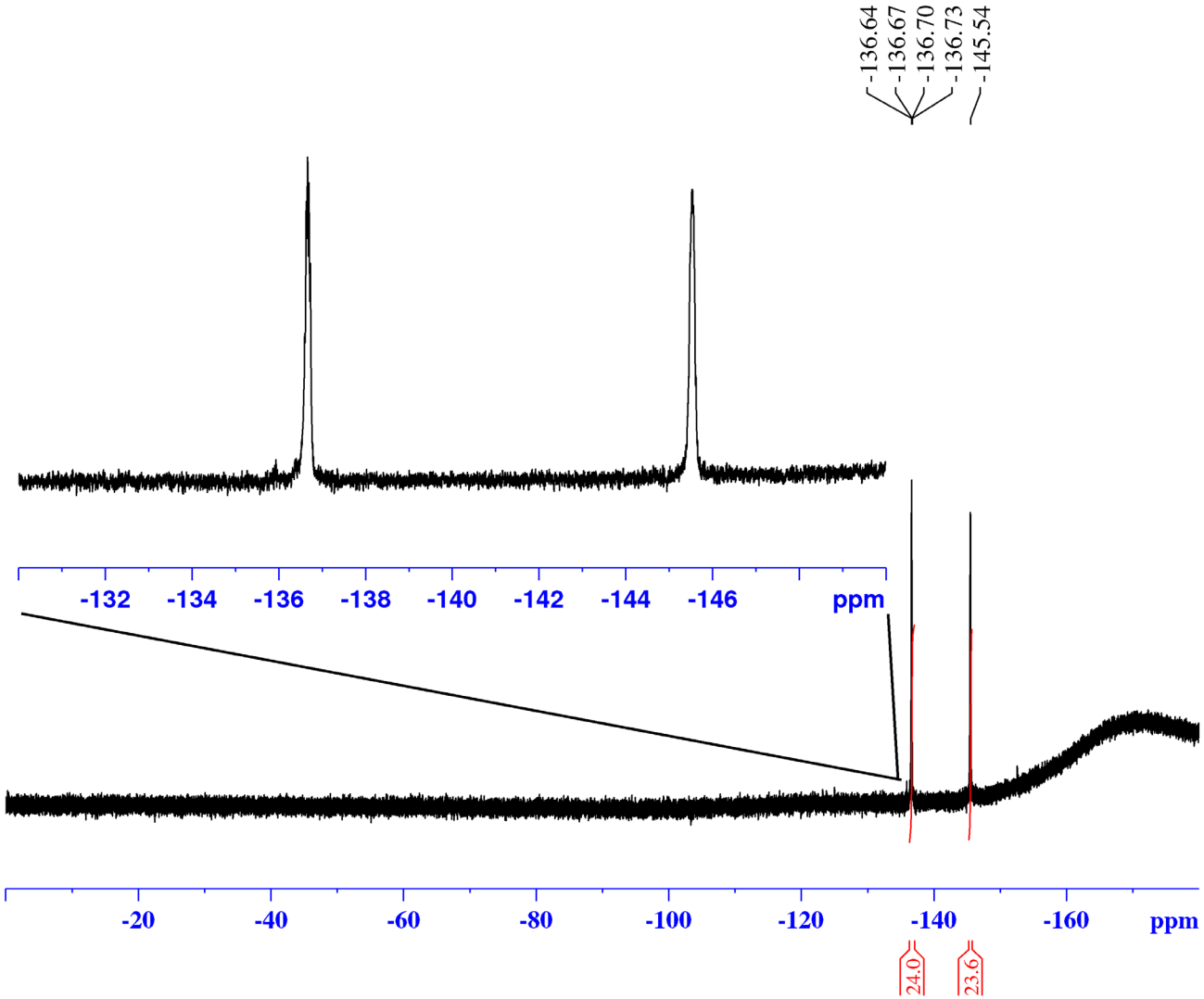
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

BRUKER

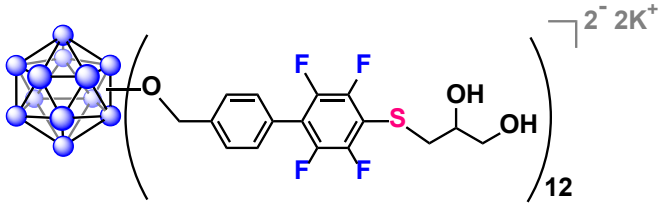


Current Data Parameters
NAME G2 Glycerol 0111 0110 (MeOD)
EXPNO 251
PROCNO 1

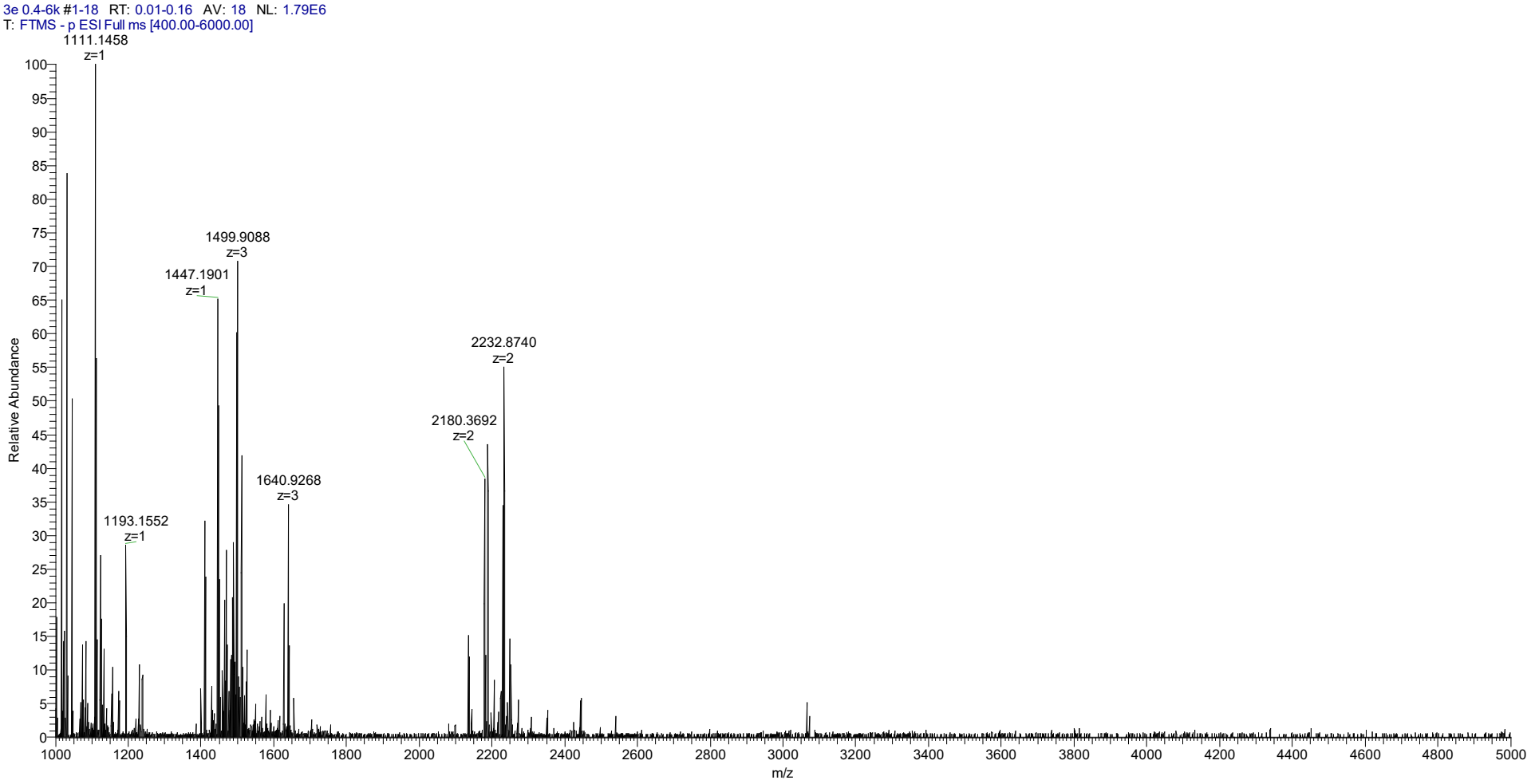
F2 - Acquisition Parameters
Date_ 20160112
Time 22.15
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

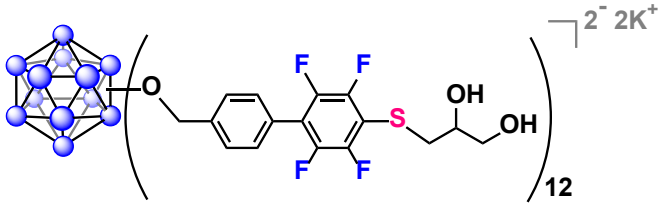
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

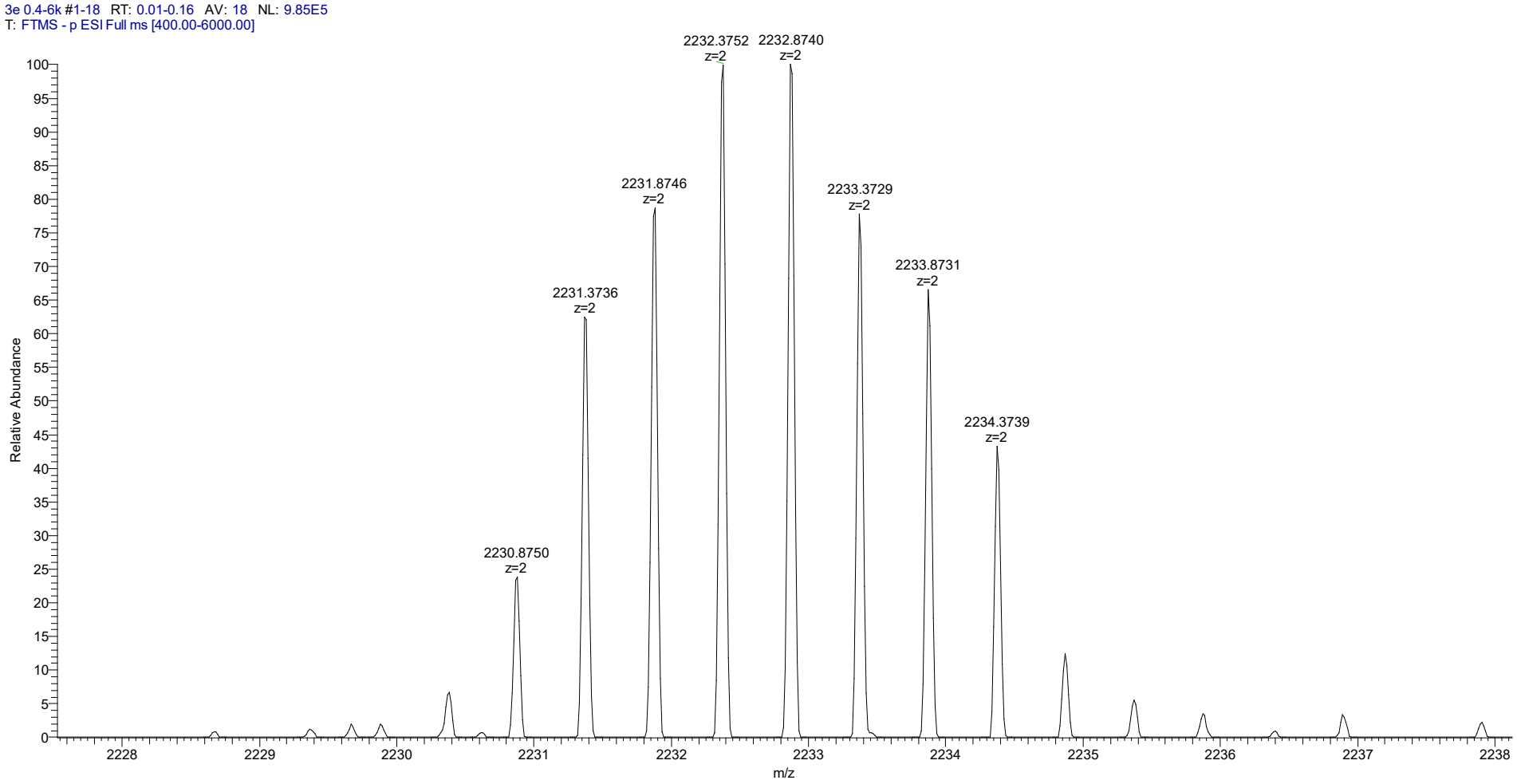


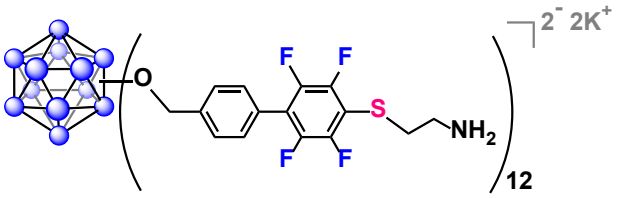
Q Exactive
High-Res Mass Spec



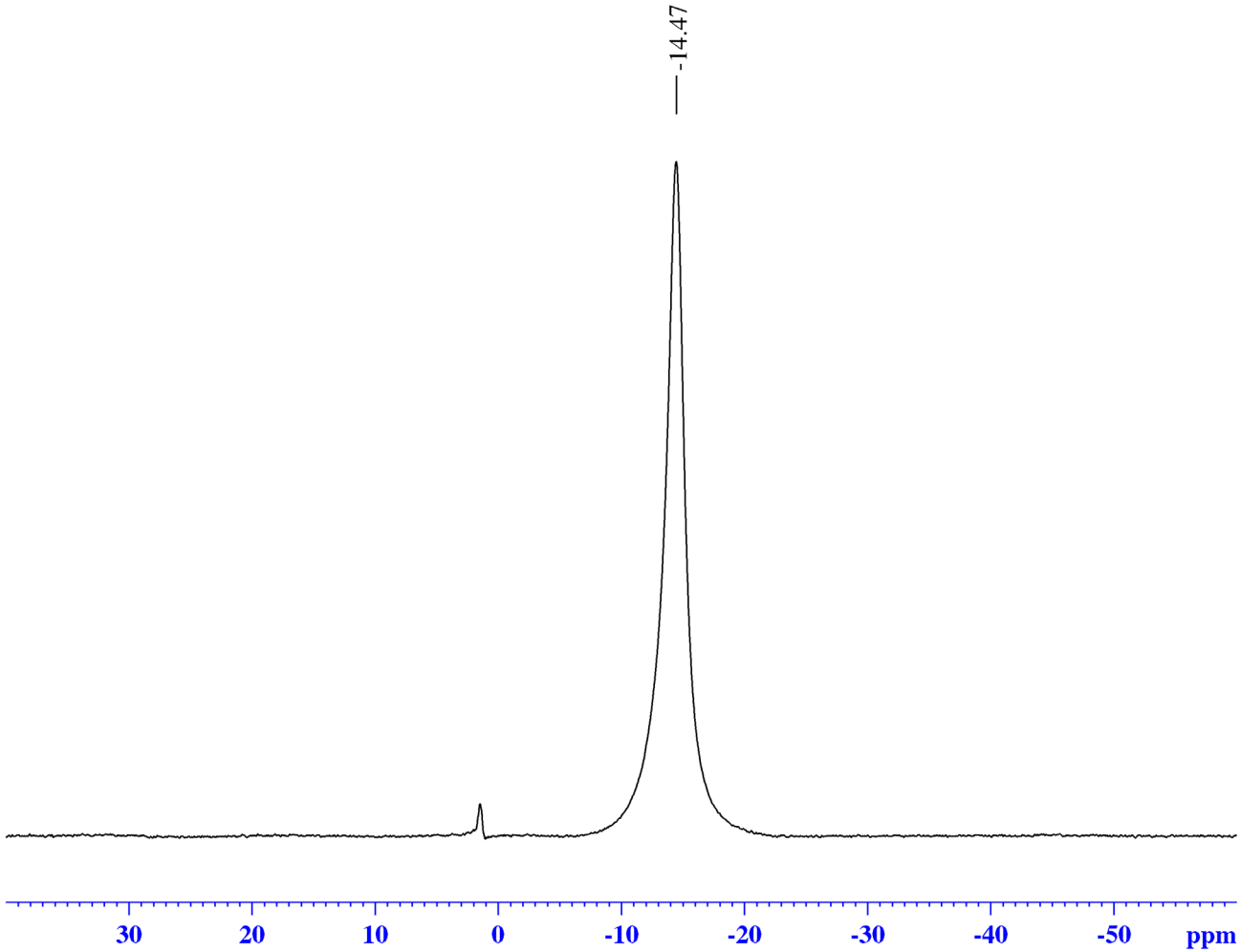


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

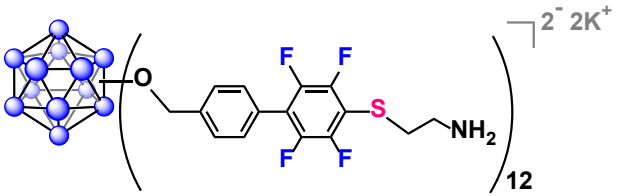


Current Data Parameters
NAME 0110
EXPNO 51
PROCNO 1

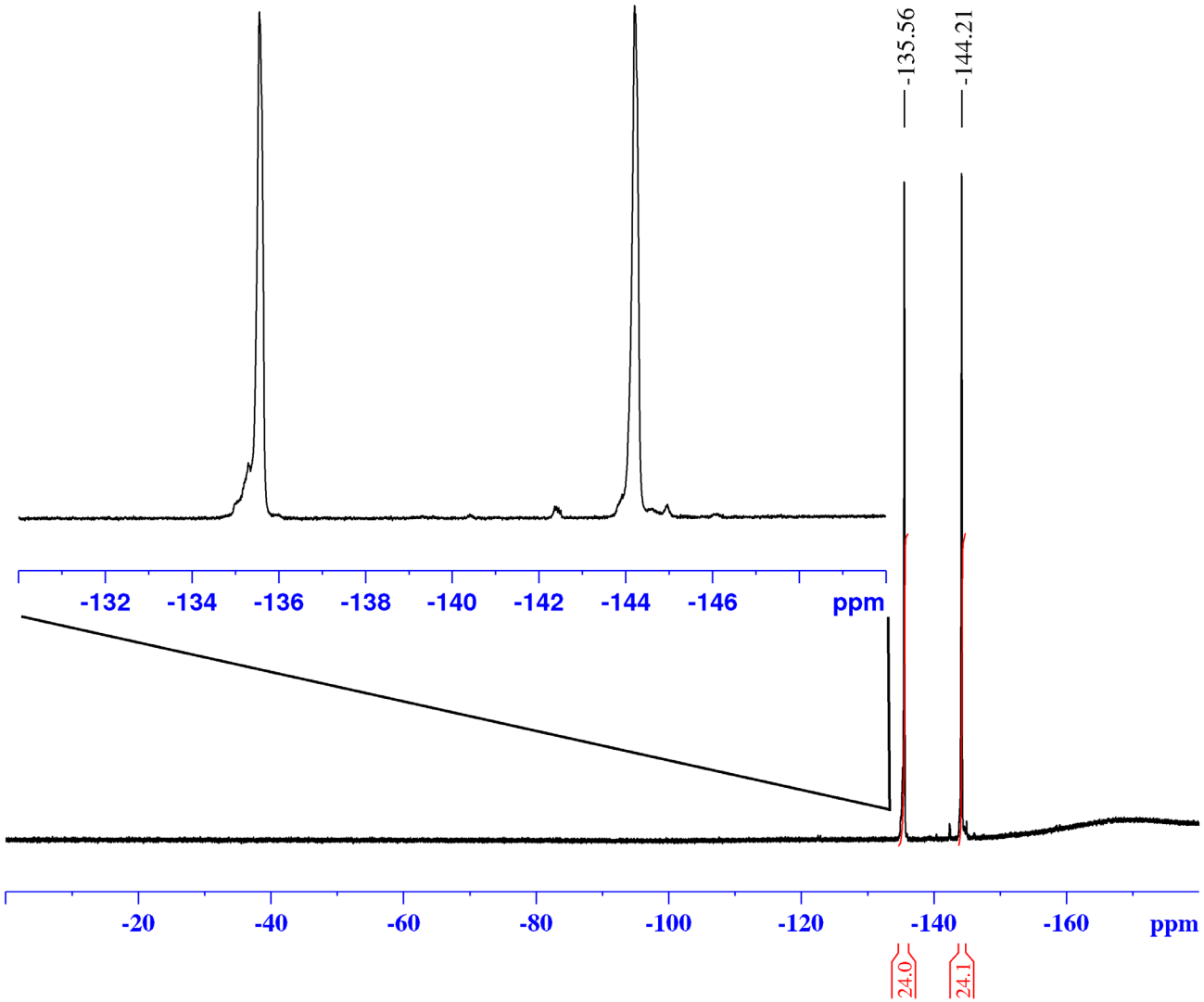
F2 - Acquisition Parameters
Date_ 20160110
Time 20.47
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

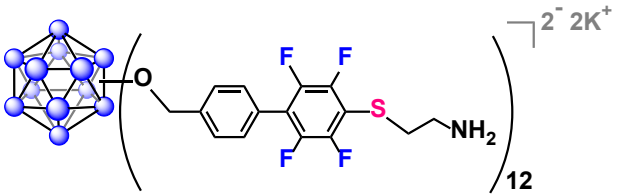


Current Data Parameters
NAME 0110
EXPNO 50
PROCNO 1

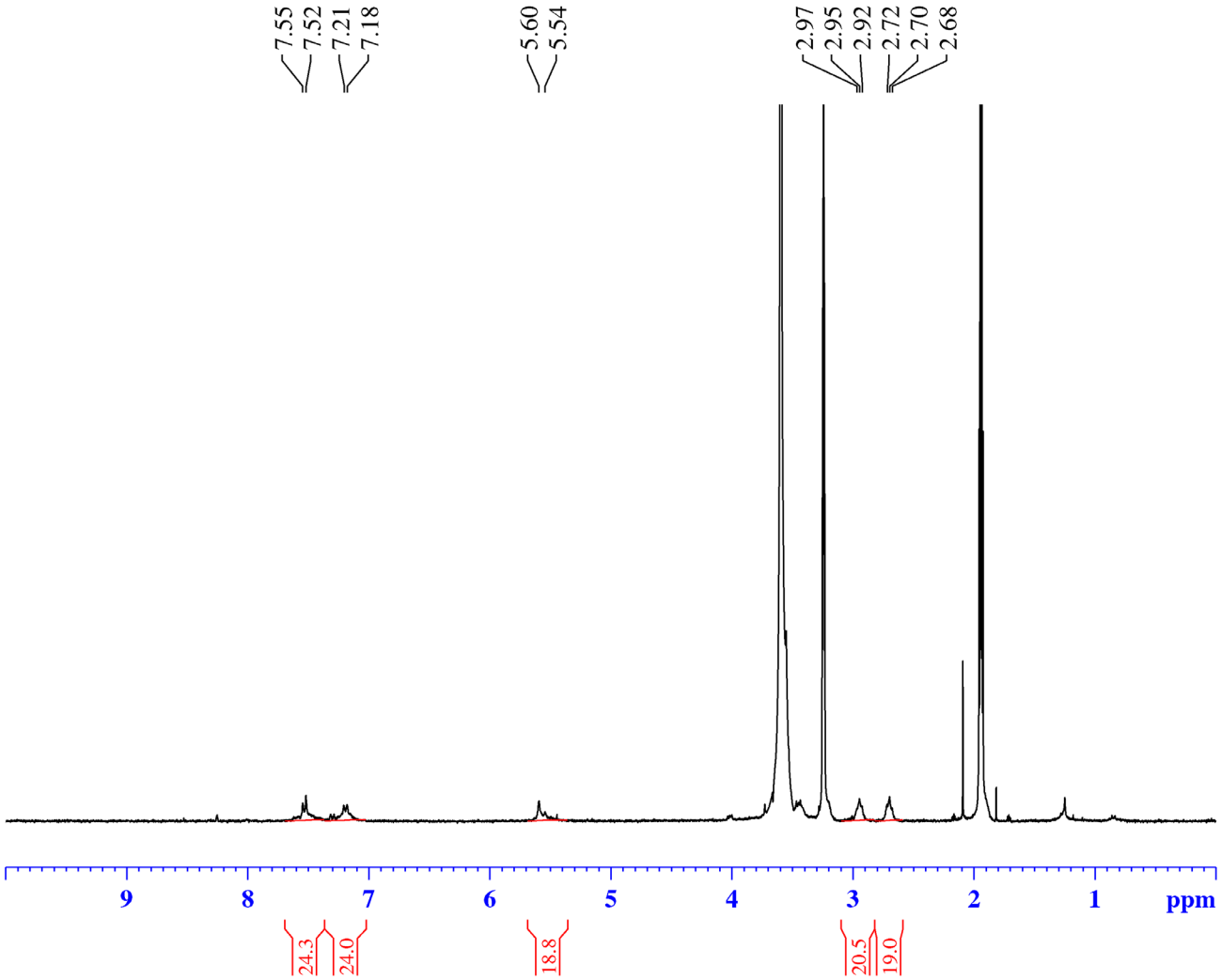
F2 - Acquisition Parameters
Date_ 20160110
Time 20.44
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

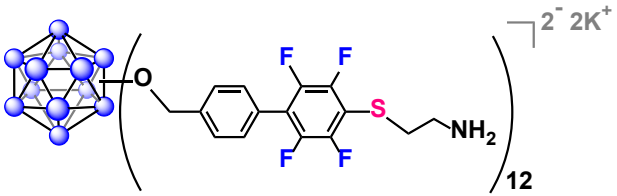


Current Data Parameters
NAME G2 CA 0112 0110 (ACN & MeOD)
EXPNO 3
PROCNO 1

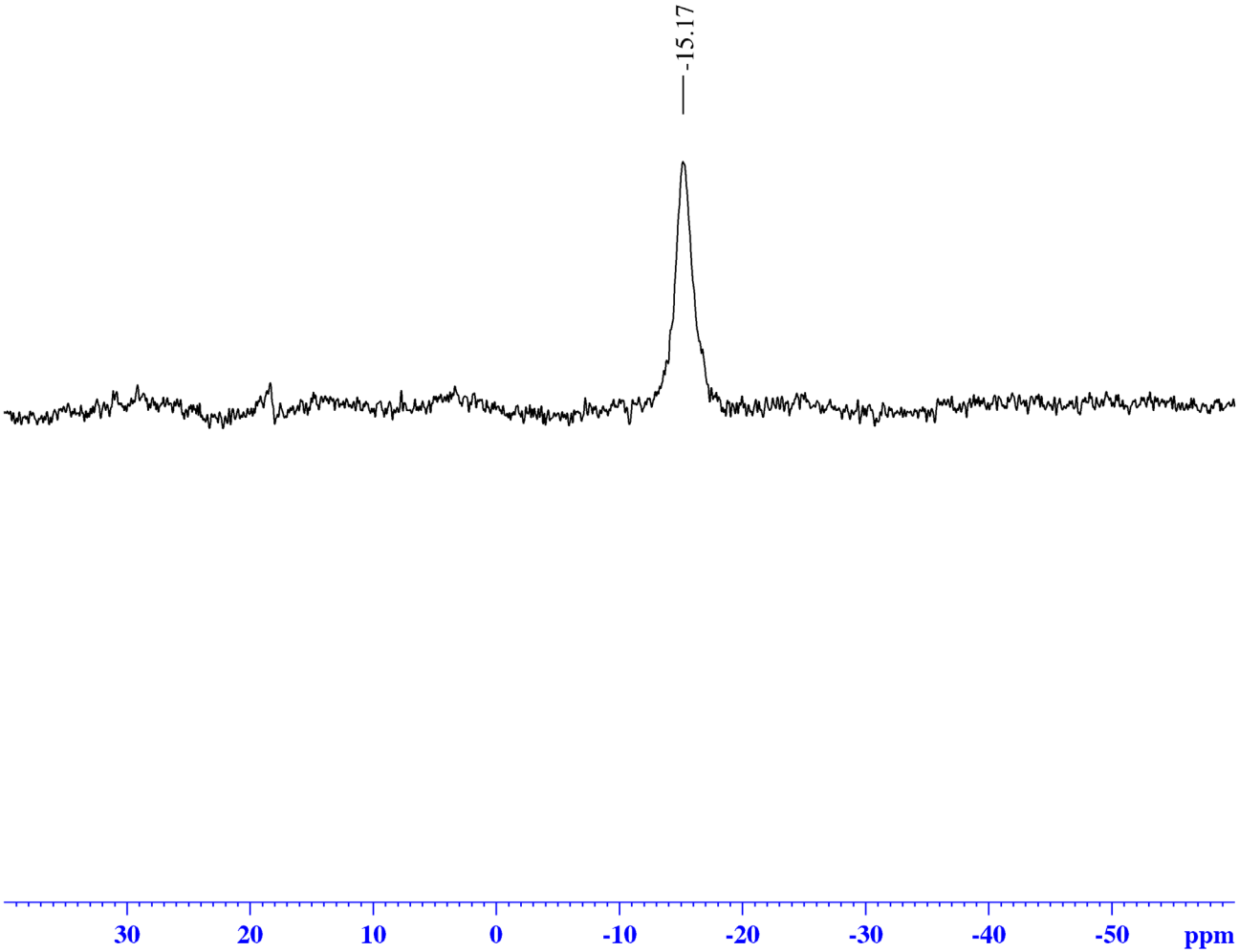
F2 - Acquisition Parameters
Date_ 20160113
Time 19.32
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.091480 Hz
AQ 5.4657025 sec
RG 574.7
DW 83.400 usec
DE 6.00 usec
TE 297.8 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 0 dB
PL1W 9.31909847 W
SFO1 300.1318008 MHz

F2 - Processing parameters
SI 65536
SF 300.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



^{11}B NMR

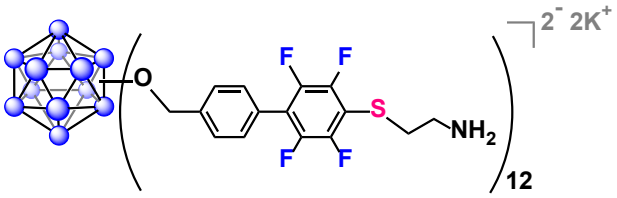


Current Data Parameters
NAME G2 CA 0112 0110 (ACN & MeOD)
EXPNO 100
PROCNO 1

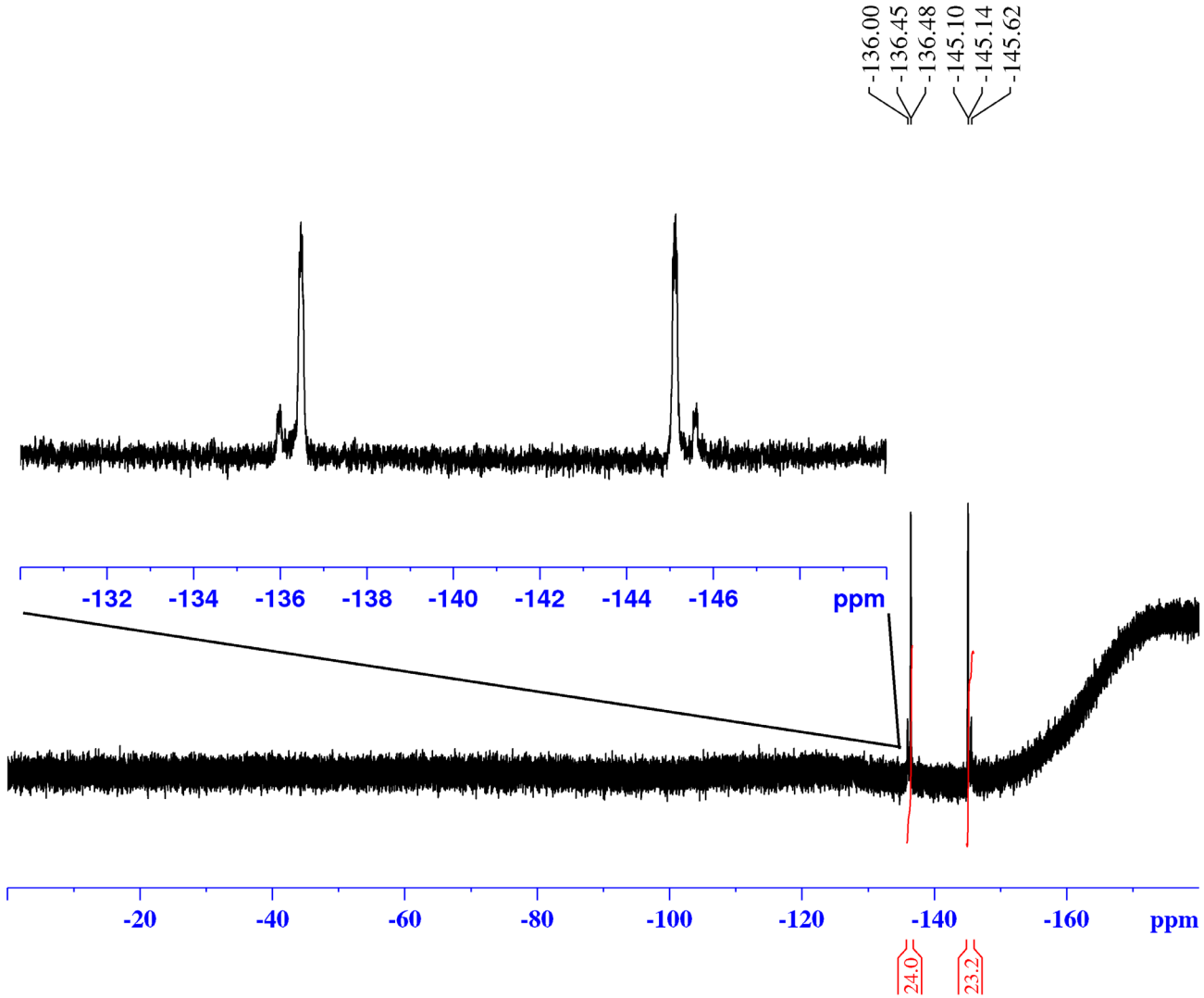
F2 - Acquisition Parameters
Date_ 20160113
Time 18.51
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

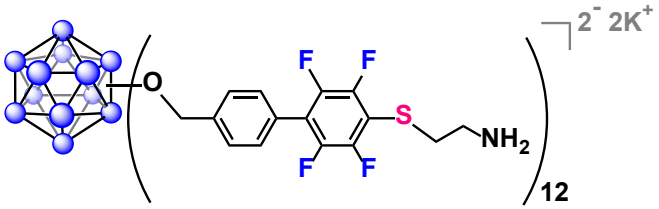


Current Data Parameters
NAME G2 CA 0112 0110 (ACN & MeOD)
EXPNO 101
PROCNO 1

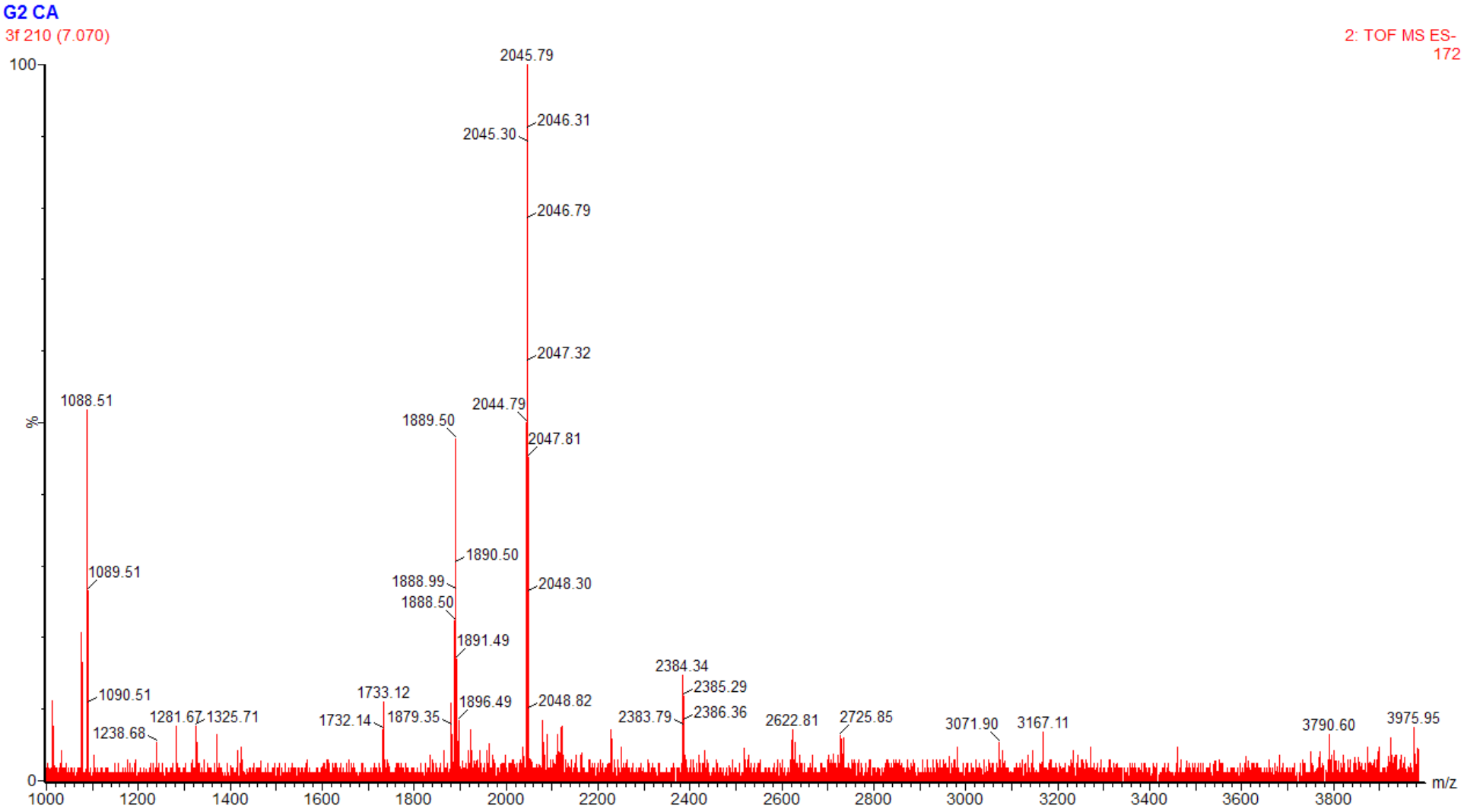
F2 - Acquisition Parameters
Date_ 20160113
Time 18.55
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

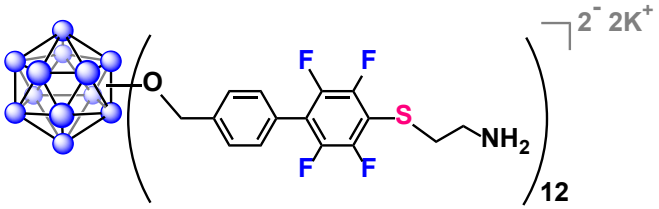
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

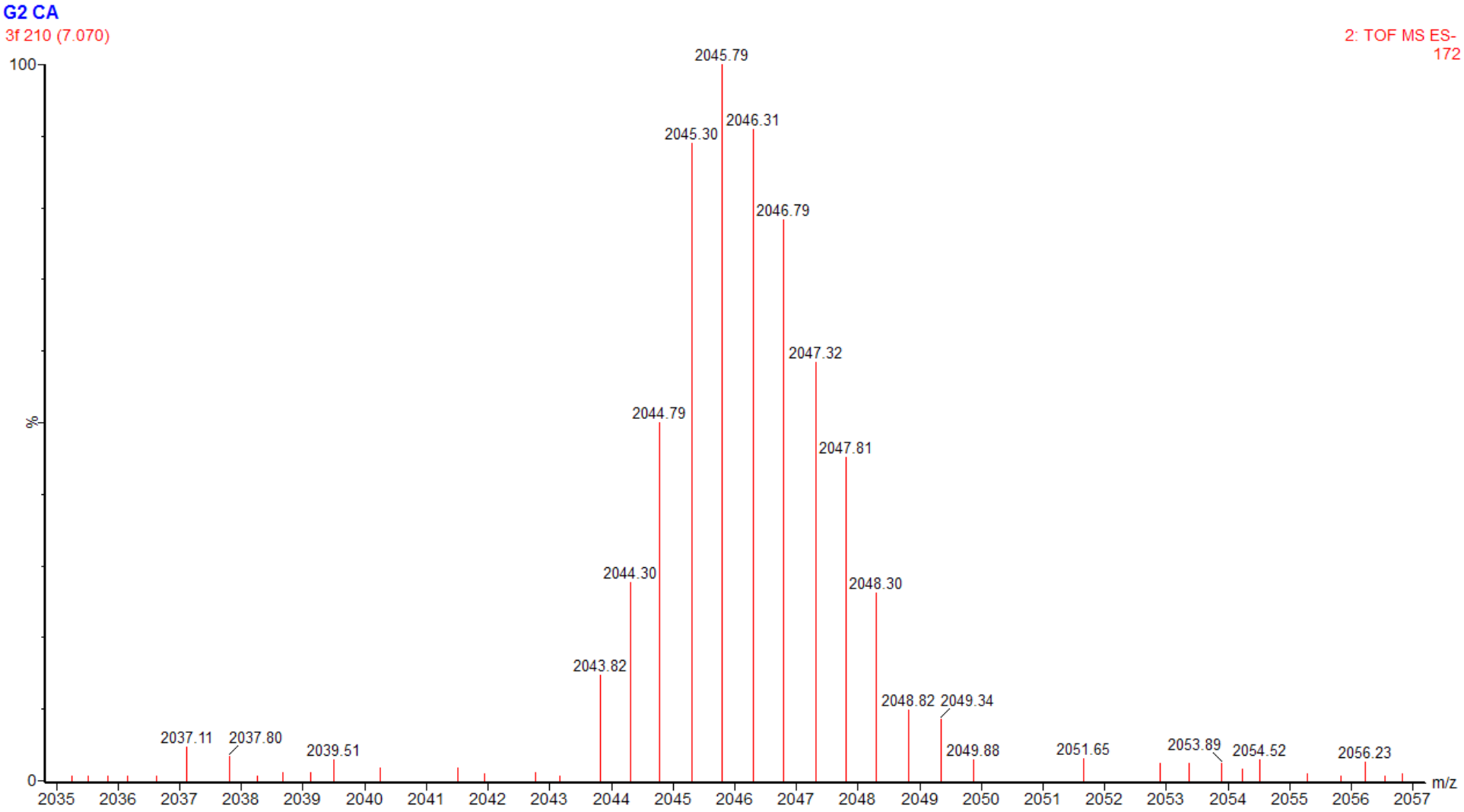


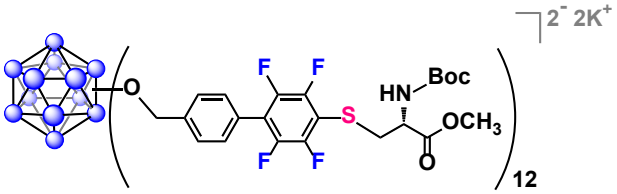
Waters Mass Spec



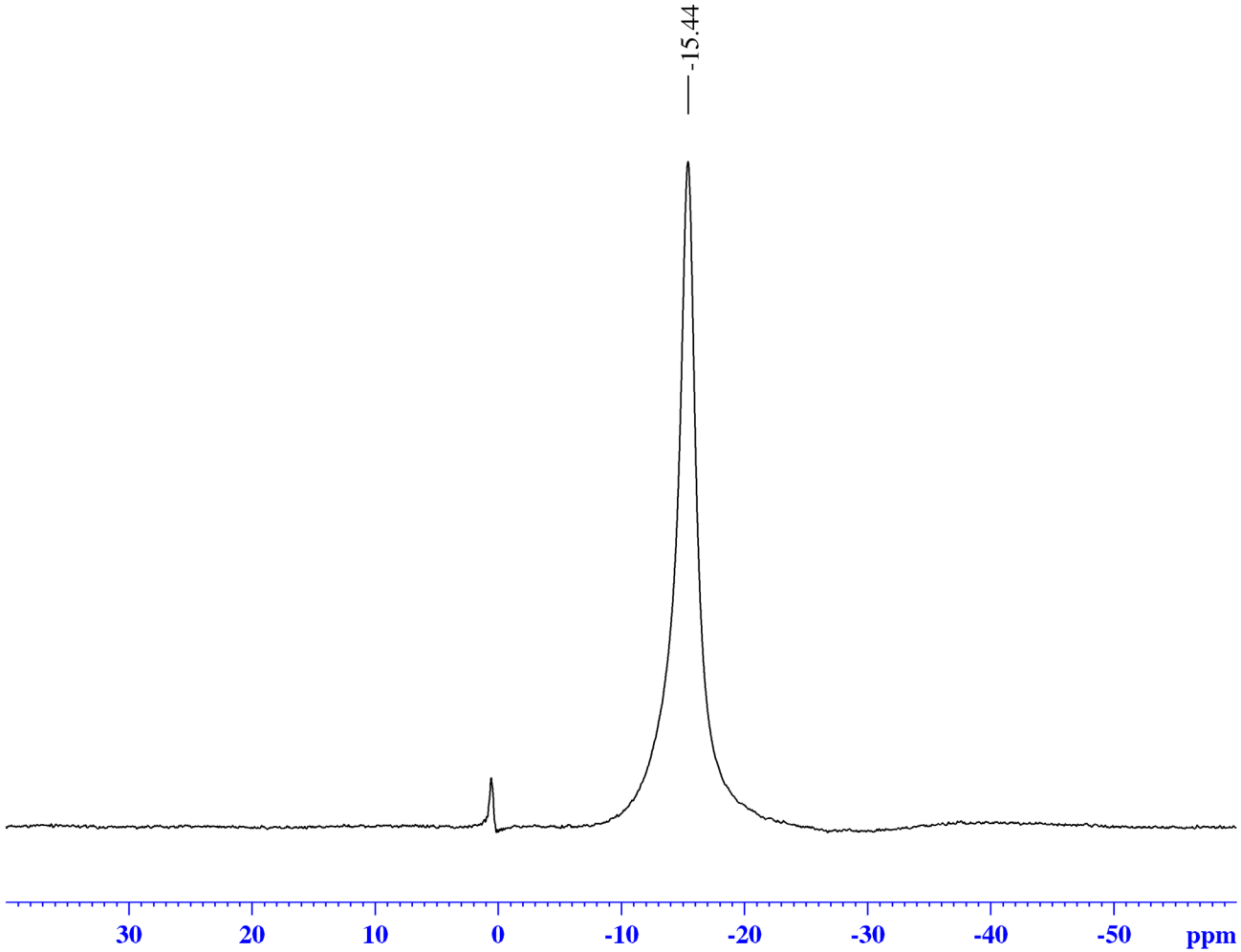


Waters Mass Spec





in situ ^{11}B NMR

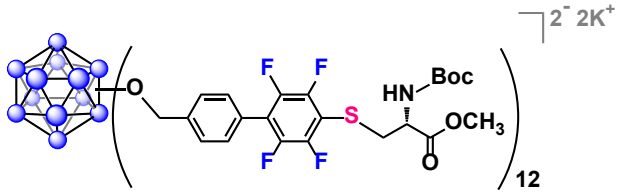


Current Data Parameters
NAME 0623
EXPNO 91
PROCNO 1

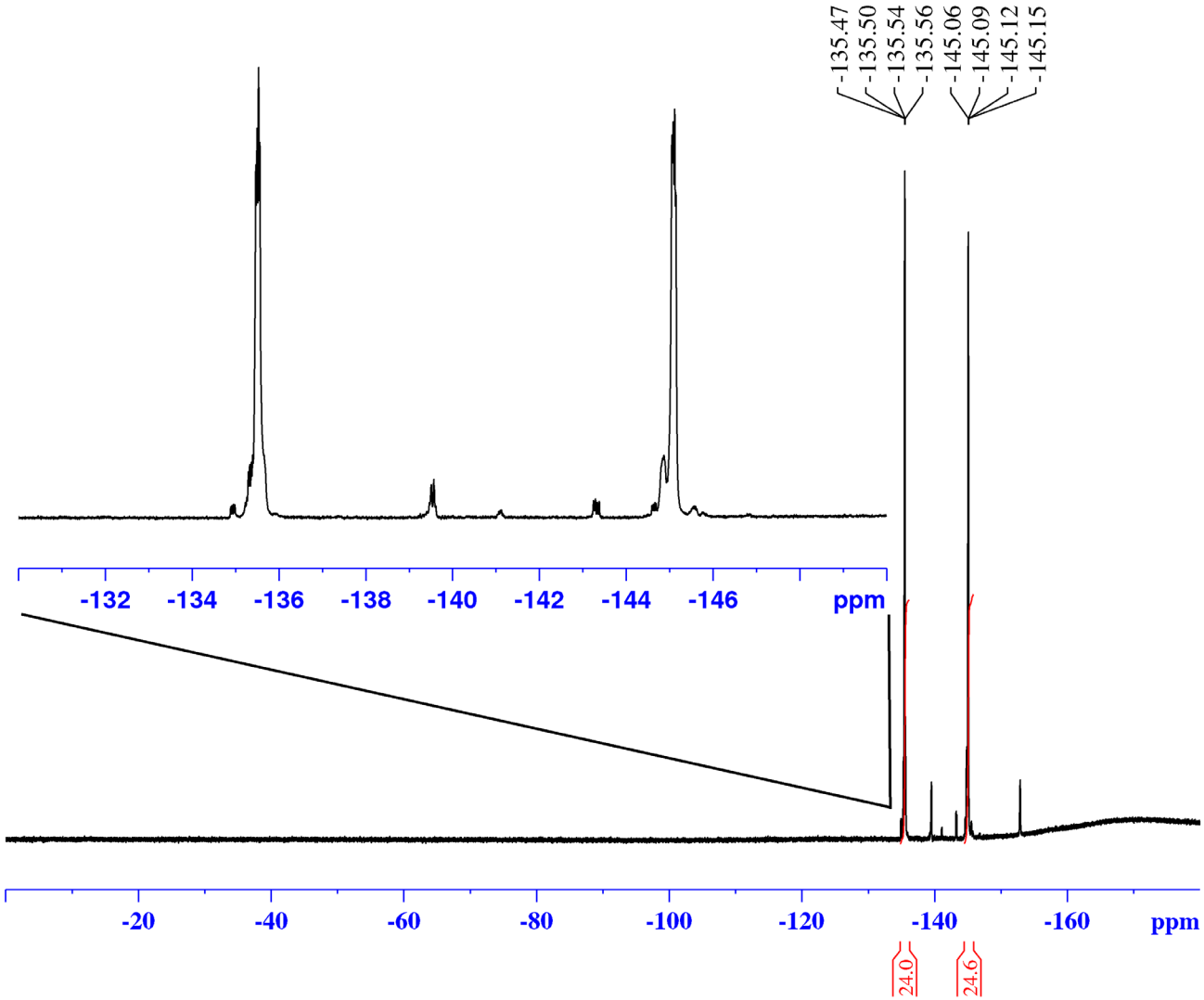
F2 - Acquisition Parameters
Date_ 20160623
Time 19.12
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

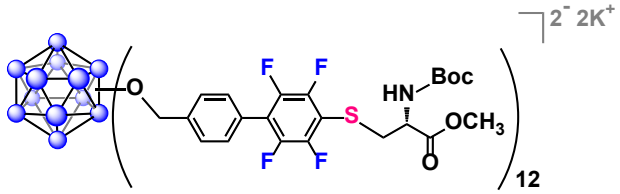


Current Data Parameters
NAME 0623
EXPNO 90
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160623
Time 19.08
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

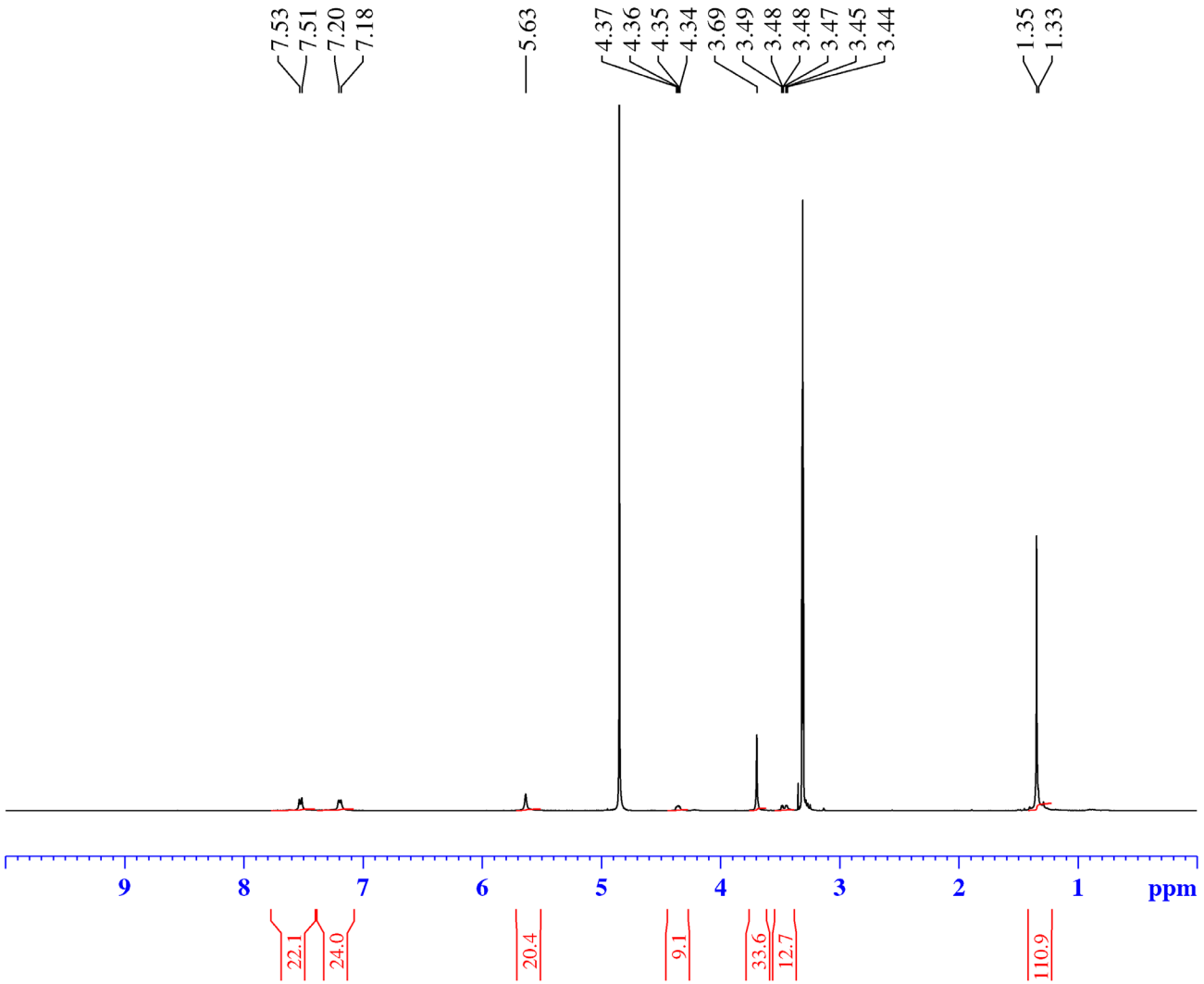
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

BRUKER

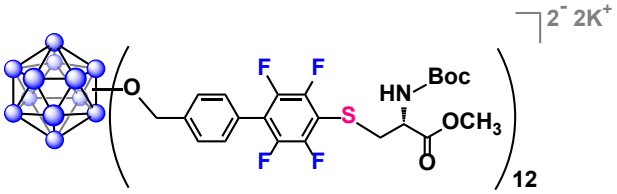


Current Data Parameters
NAME G2 BC 0630 0623 (MeOD)
EXPNO 50
PROCNO 1

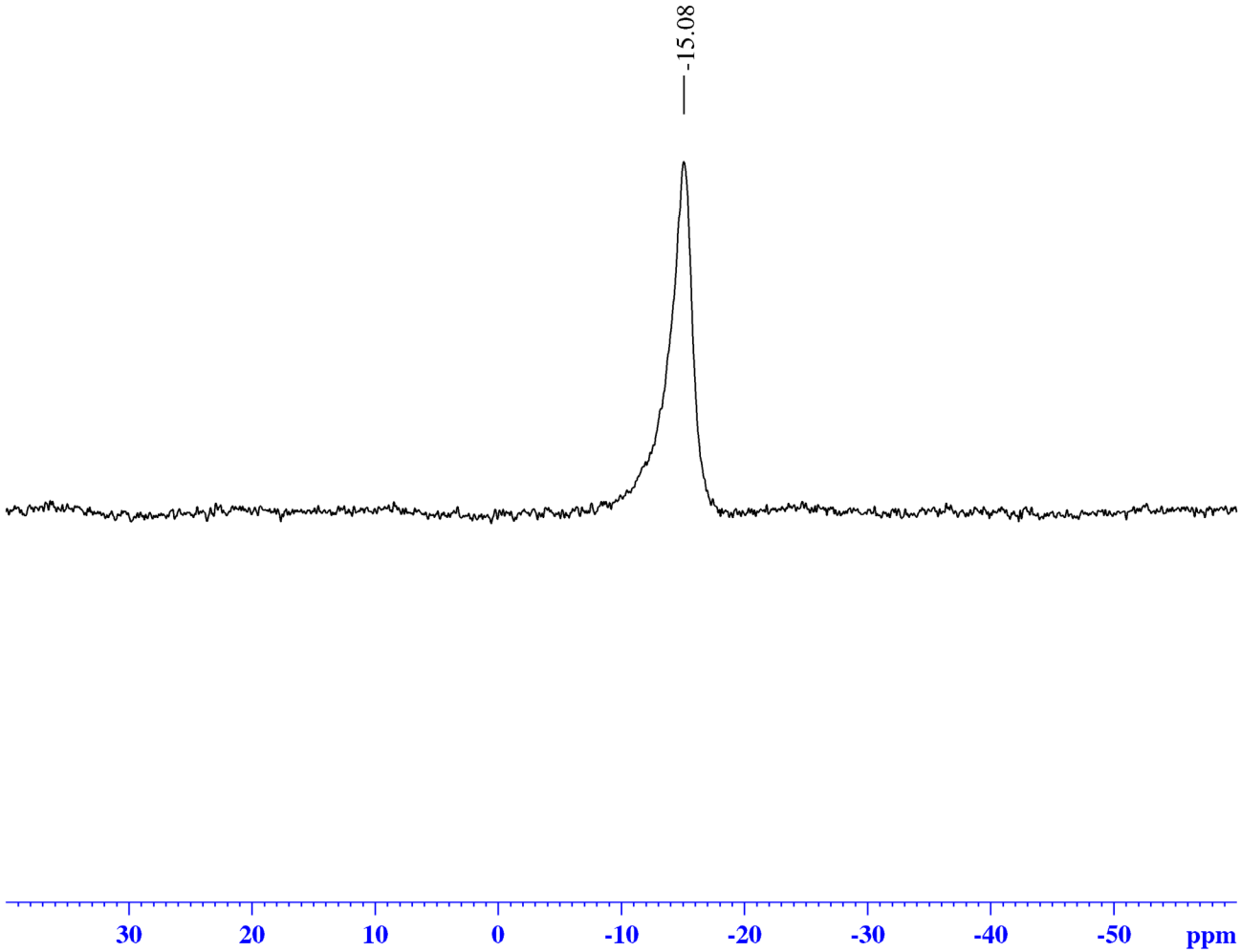
F2 - Acquisition Parameters
Date_ 20160630
Time 19.48
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

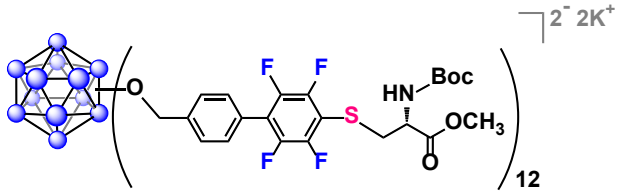


Current Data Parameters
NAME G2 BC 0630 0623 (MeOD)
EXPNO 52
PROCNO 1

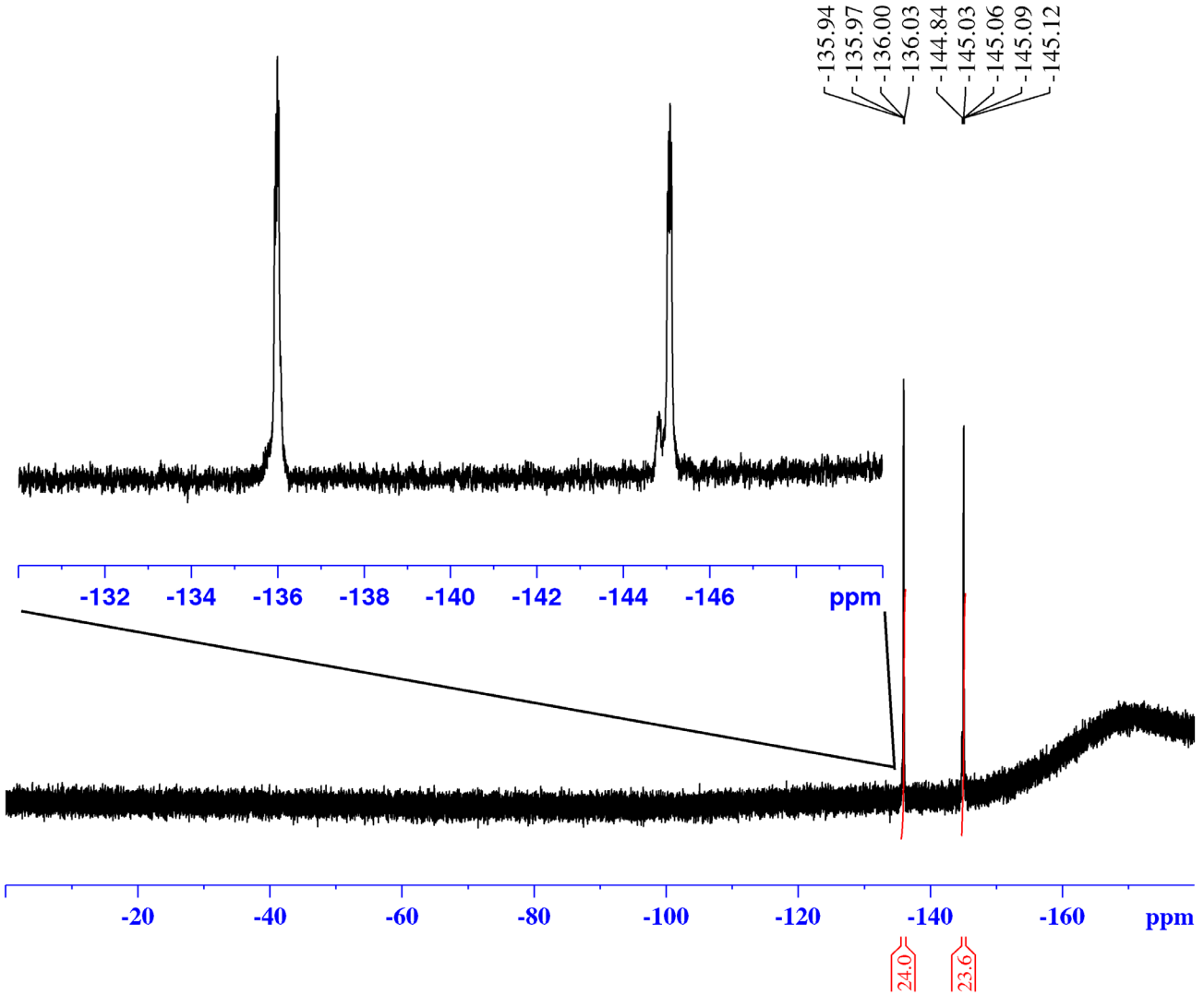
F2 - Acquisition Parameters
Date_ 20160630
Time 19.54
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

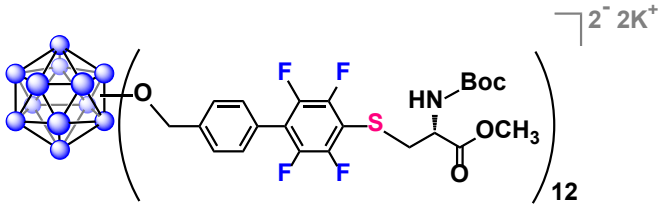


Current Data Parameters
NAME G2 BC 0630 0623 (MeOD)
EXPNO 51
PROCNO 1

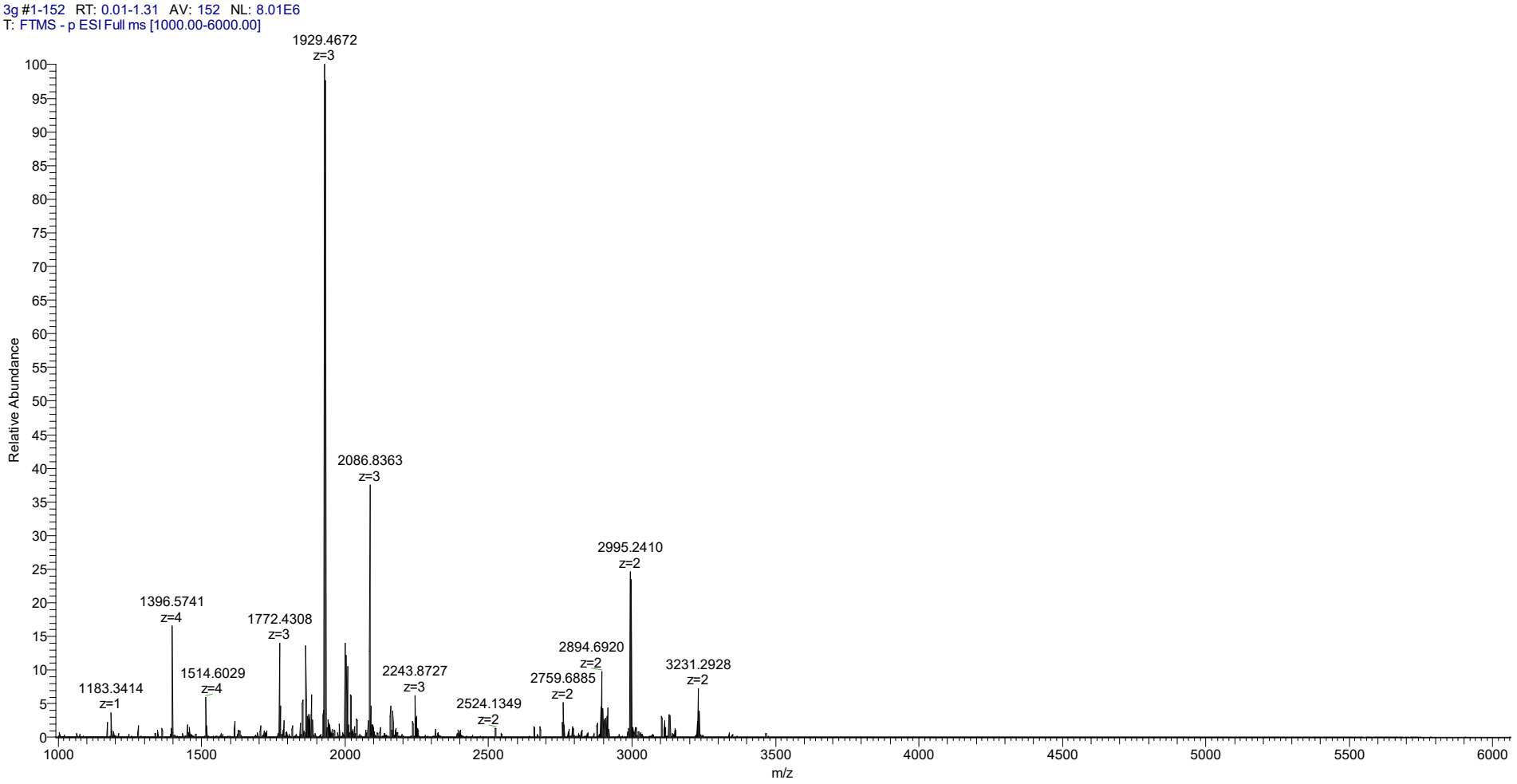
F2 - Acquisition Parameters
Date_ 20160630
Time 19.50
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 32
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

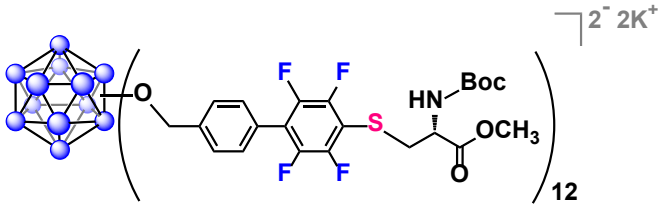
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



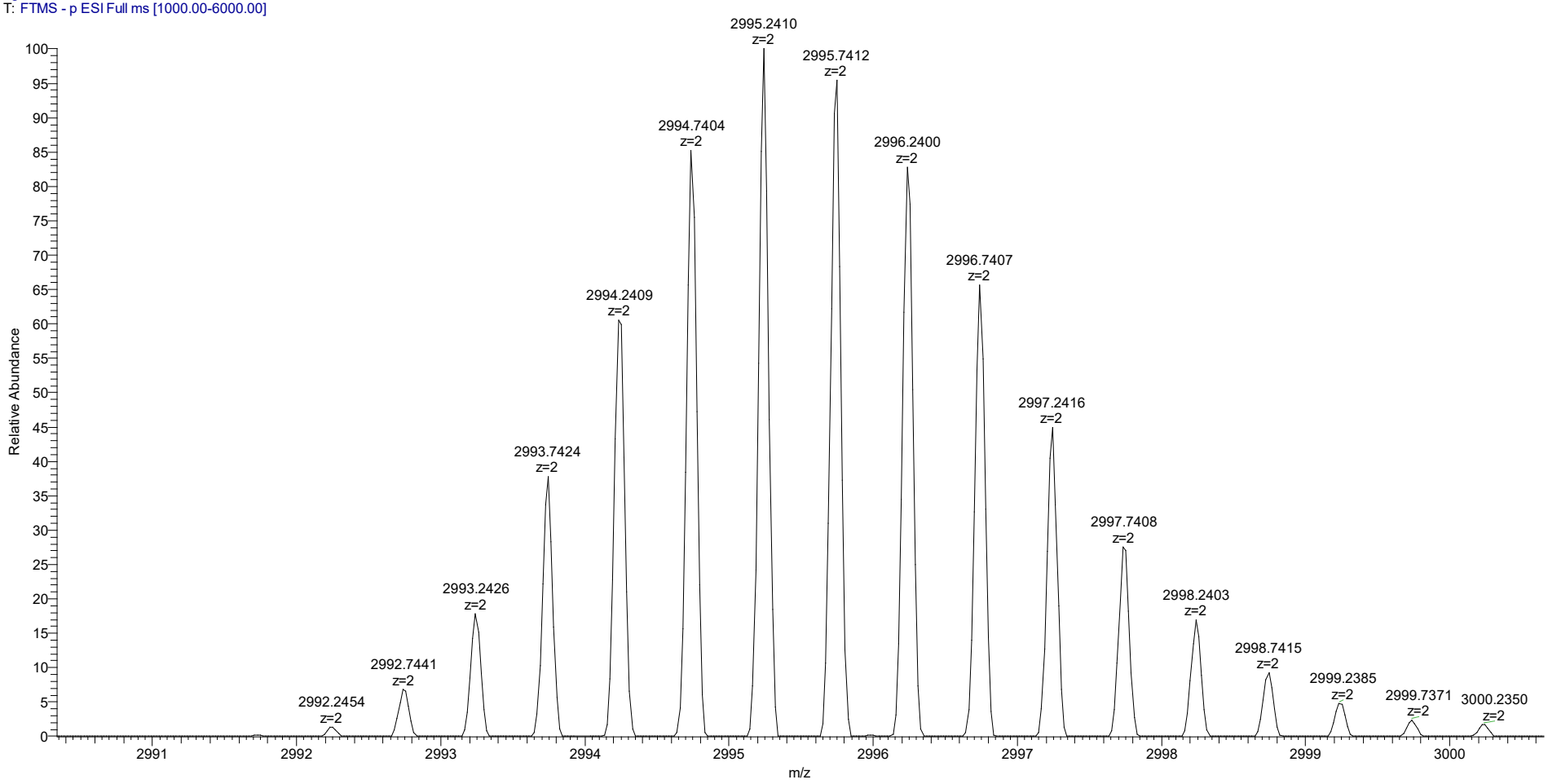
Q Exactive
High-Res Mass Spec

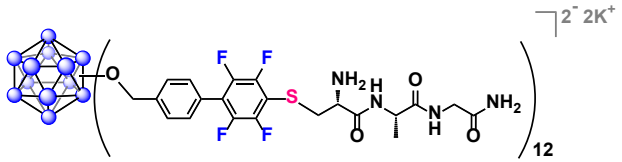




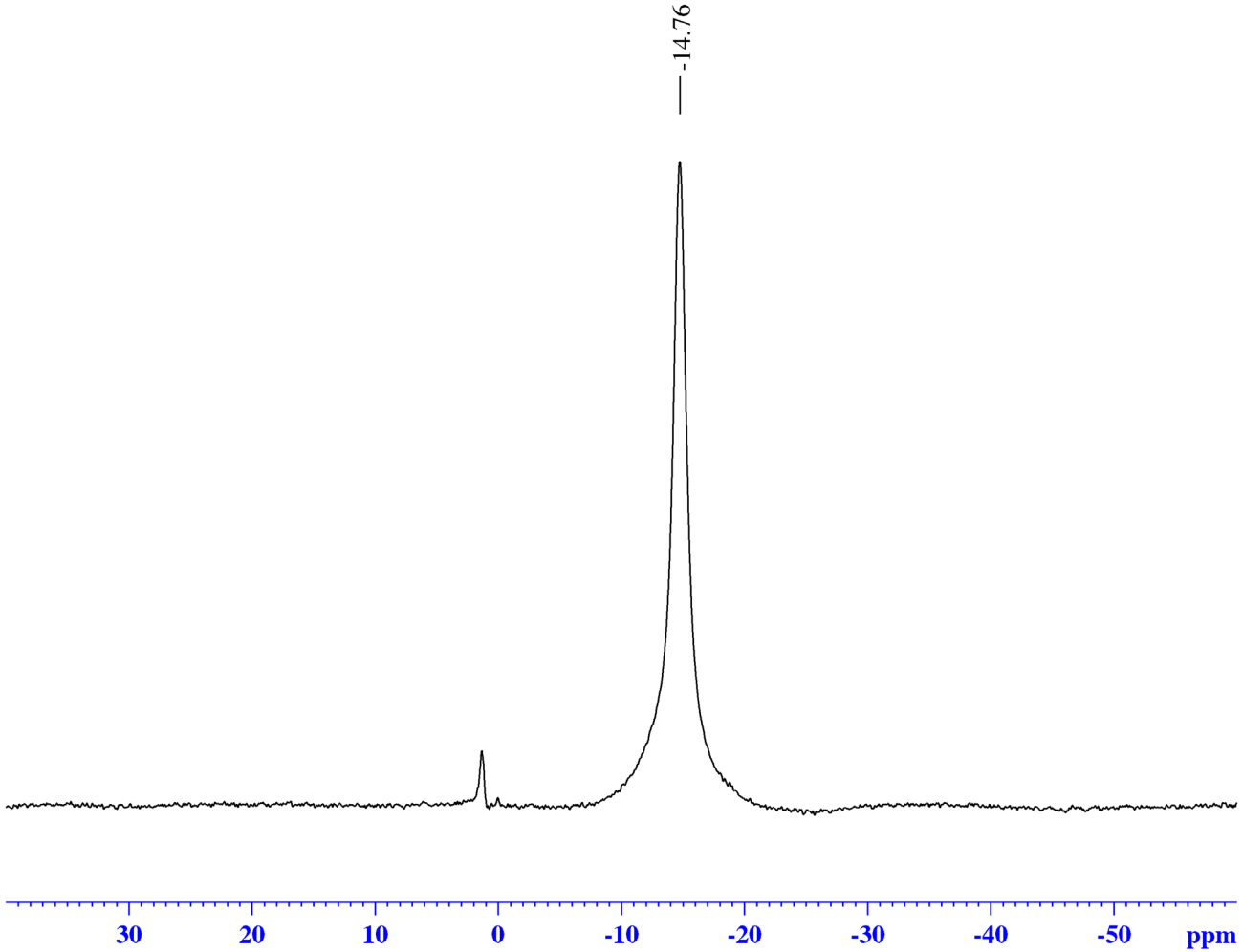
Q Exactive
High-Res Mass Spec

3g #1-152 RT: 0.01-1.31 AV: 152 NL: 1.97E6
T: FTMS - p ESI Full ms [1000.00-6000.00]





in situ ^{11}B NMR

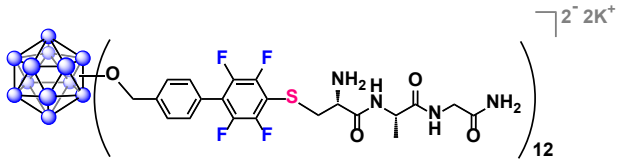


Current Data Parameters
NAME 0520
EXPNO 131
PROCNO 1

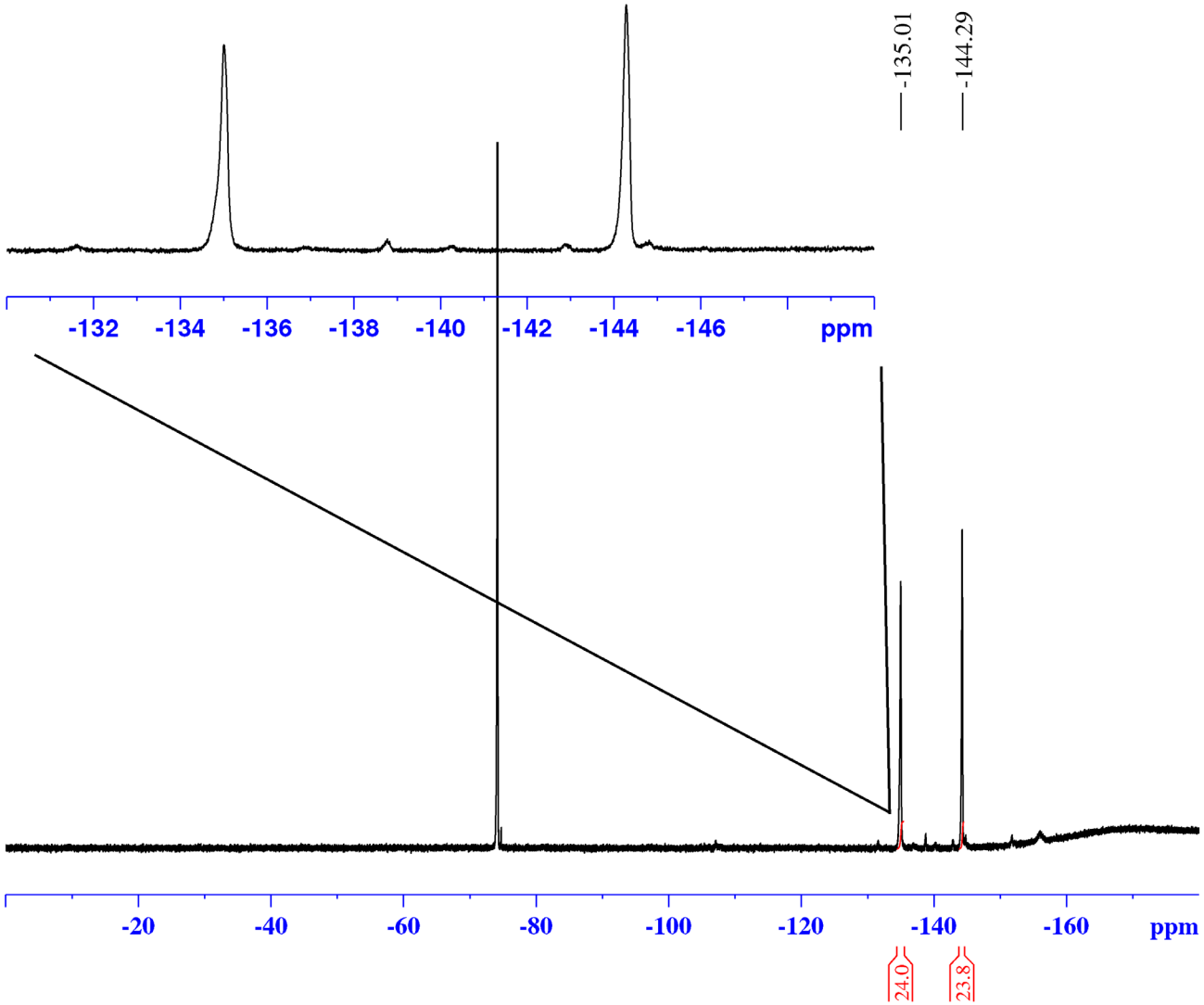
F2 - Acquisition Parameters
Date_ 20160520
Time 21.13
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

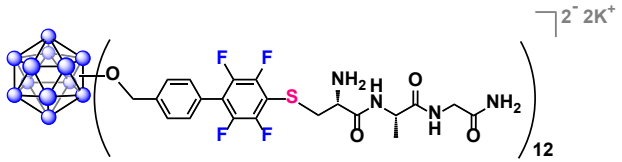


Current Data Parameters
NAME 0520
EXPNO 130
PROCNO 1

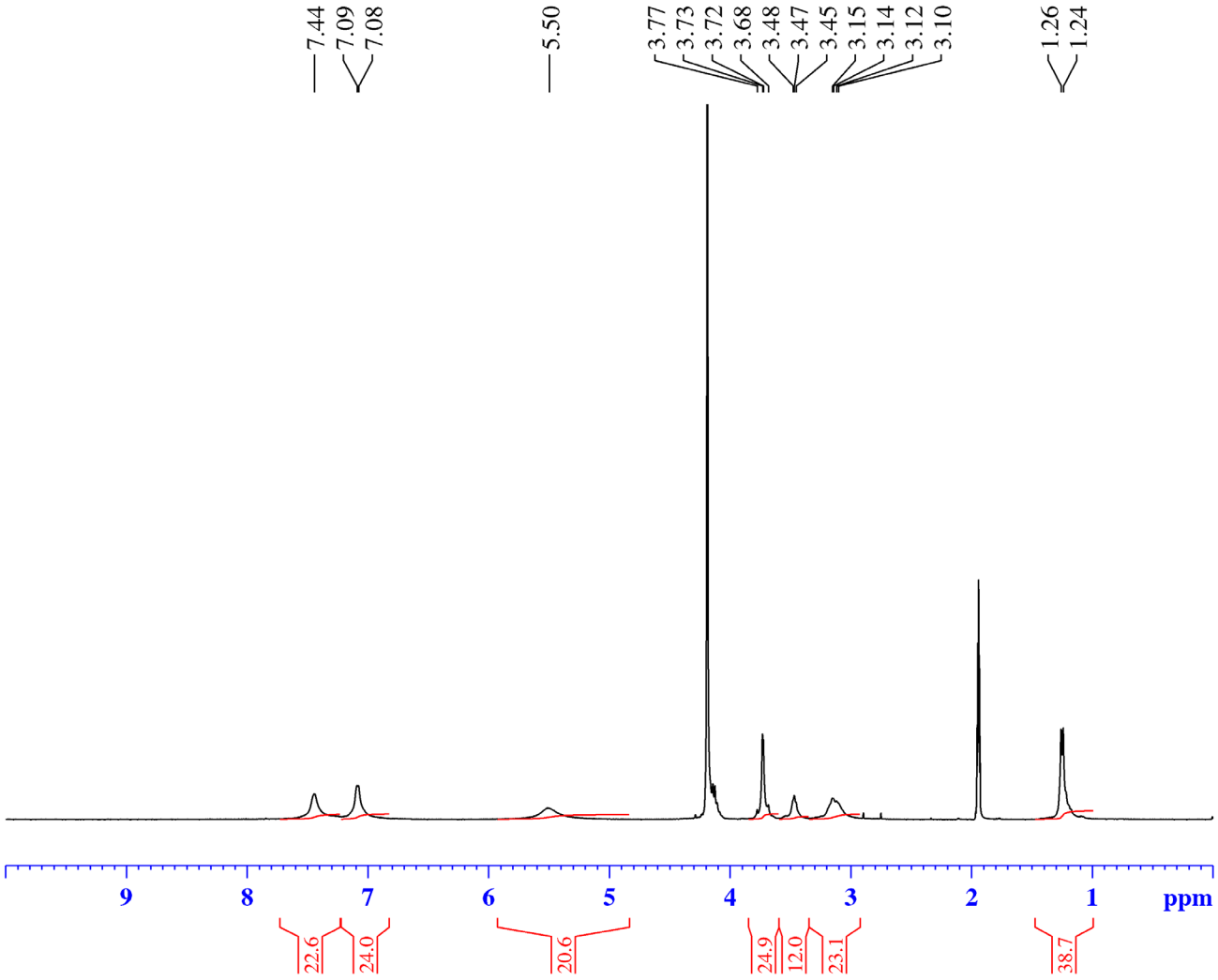
F2 - Acquisition Parameters
Date_ 20160520
Time 21.10
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

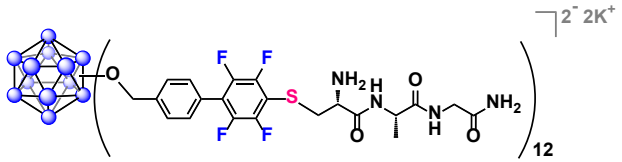


Current Data Parameters
NAME G2 CAG 0620 0520 (ACN & D2O)
EXPNO 80
PROCNO 1

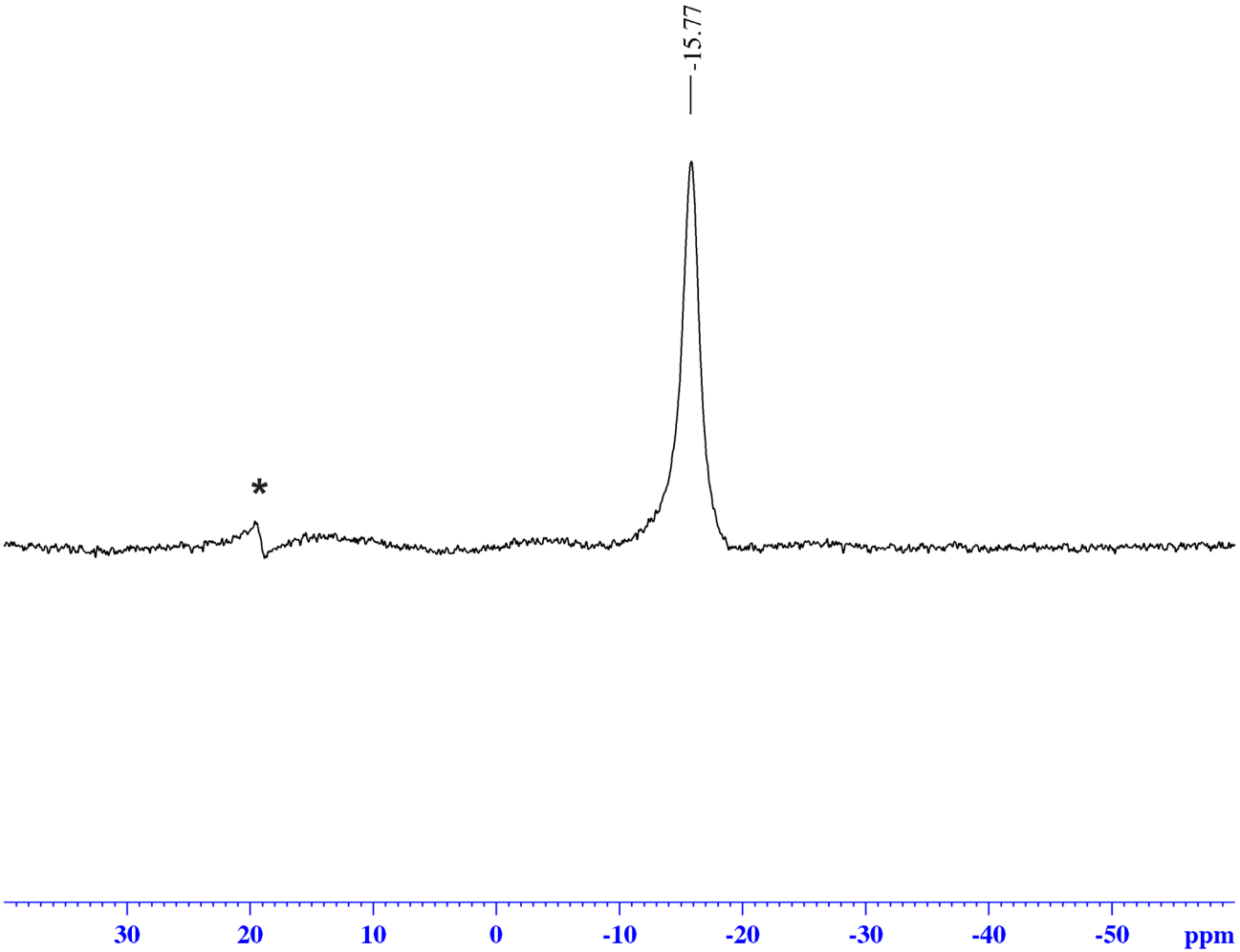
F2 - Acquisition Parameters
Date_ 20160622
Time 16.18
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CD3CN
NS 64
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1290946 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR



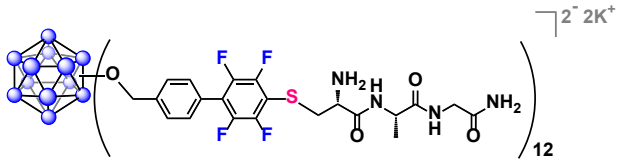
Current Data Parameters
NAME G2 CAG 0620 0520 (ACN & D2O)
EXPNO 82
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160622
Time 16.25
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT CD3CN
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

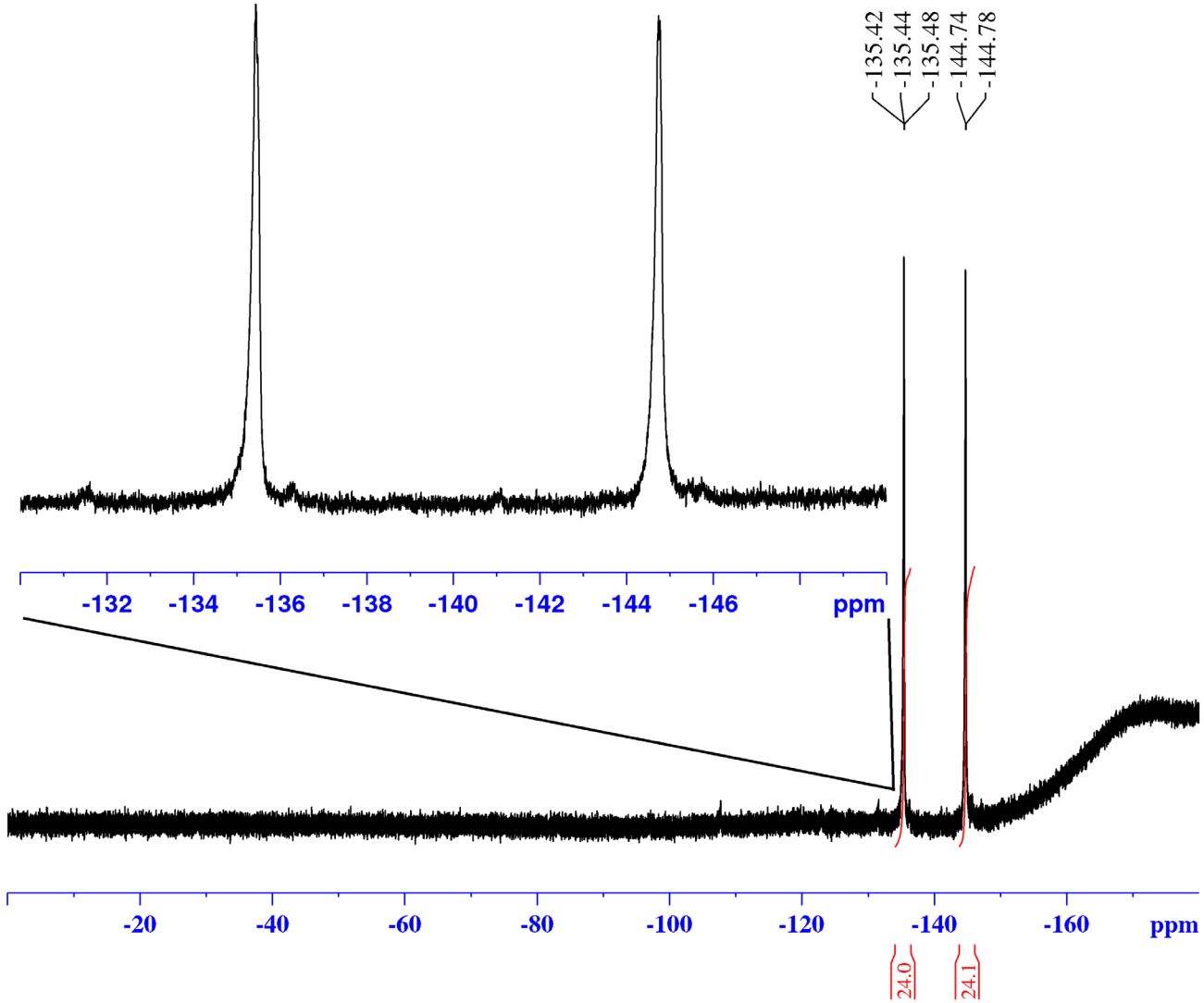
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3773553 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

* This peak corresponds to a small boric aicd impurity.



^{19}F NMR

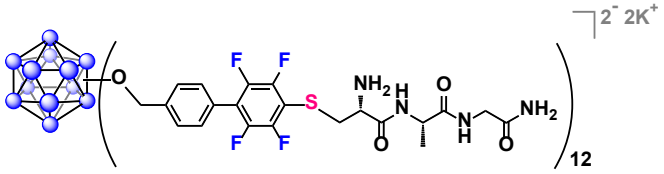


Current Data Parameters
NAME G2 CAG 0620 0520 (ACN & D2O)
EXPNO 81
PROCNO 1

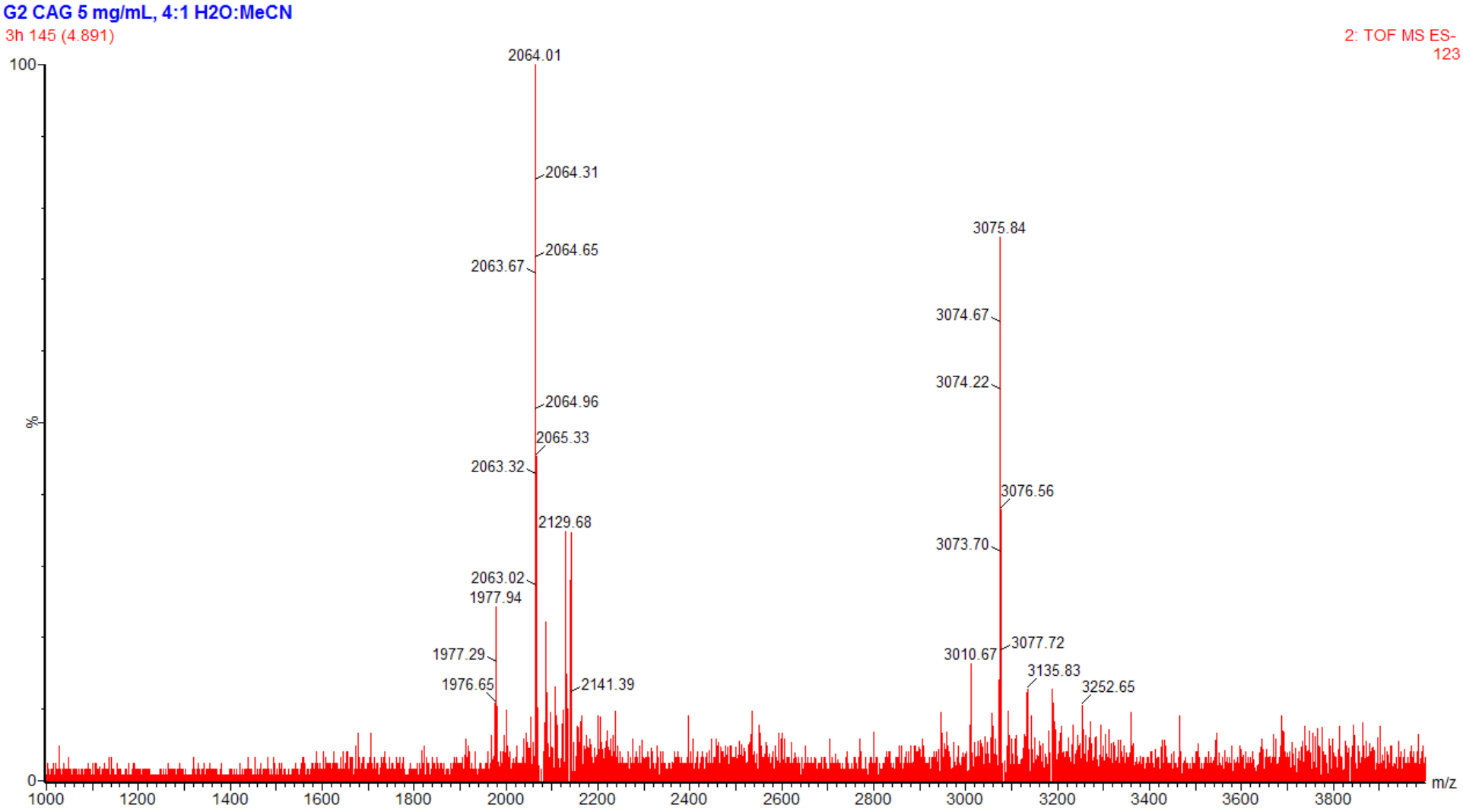
F2 - Acquisition Parameters
Date_ 20160622
Time 16.22
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

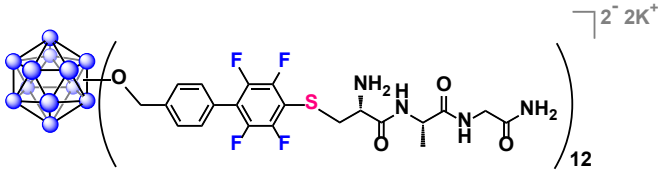
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4975772 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

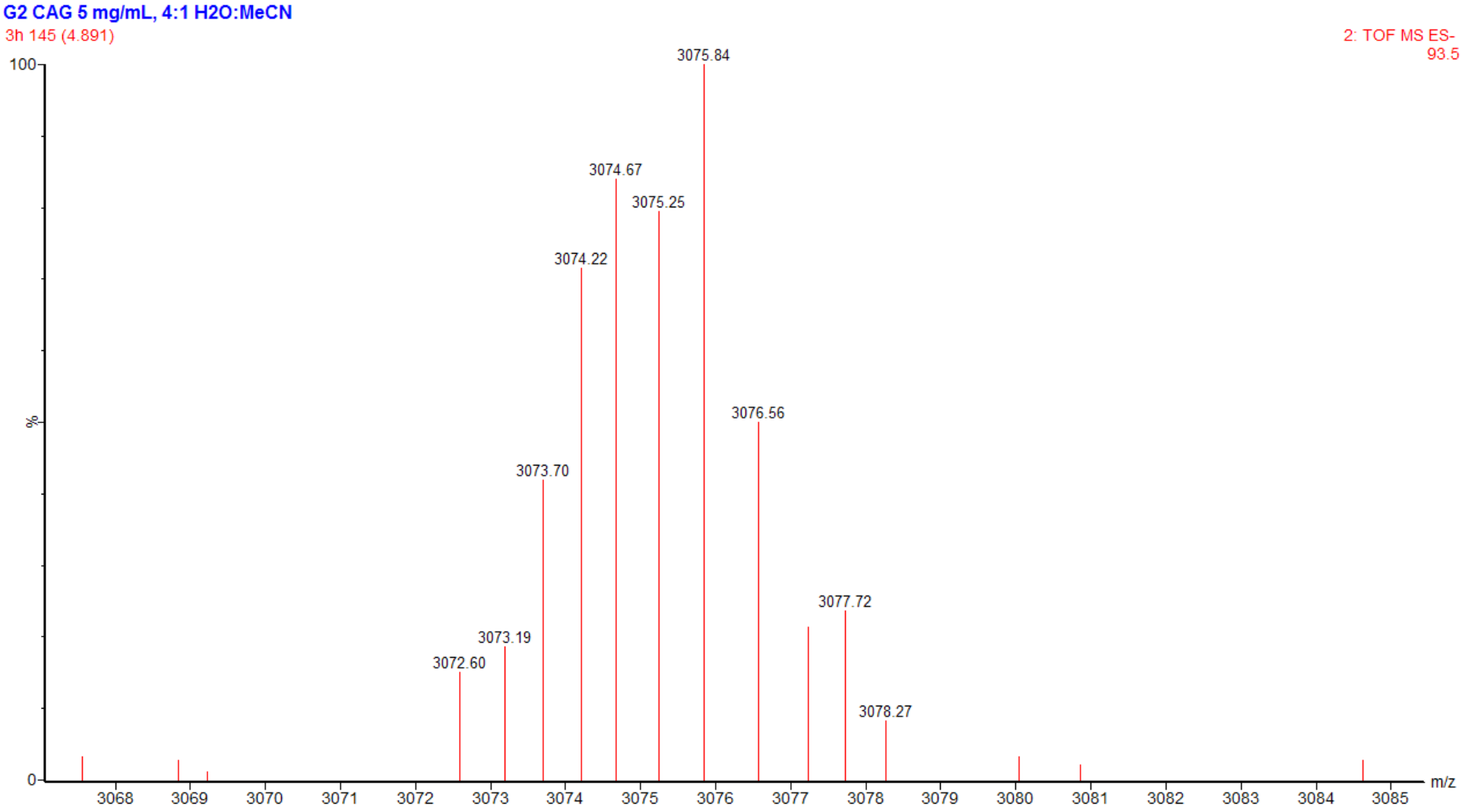


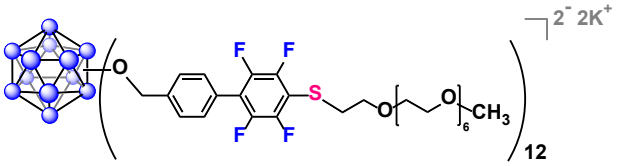
Waters Mass Spec



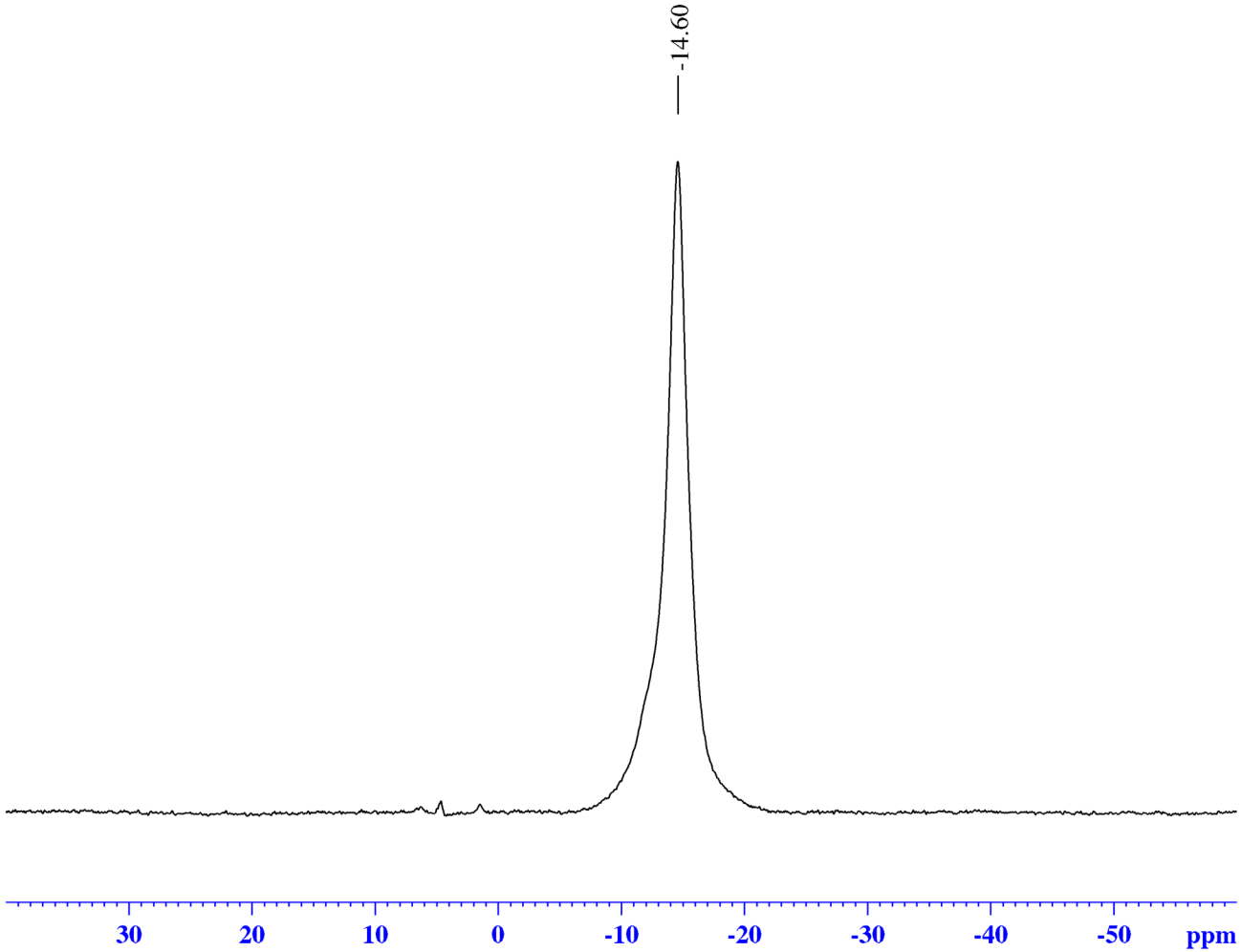


Waters Mass Spec





in situ ^{11}B NMR

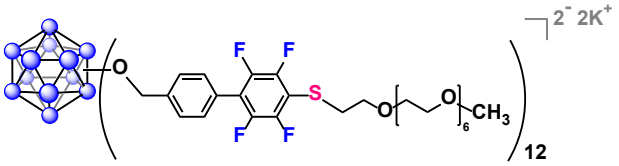


Current Data Parameters
NAME 1209
EXPNO 111
PROCNO 1

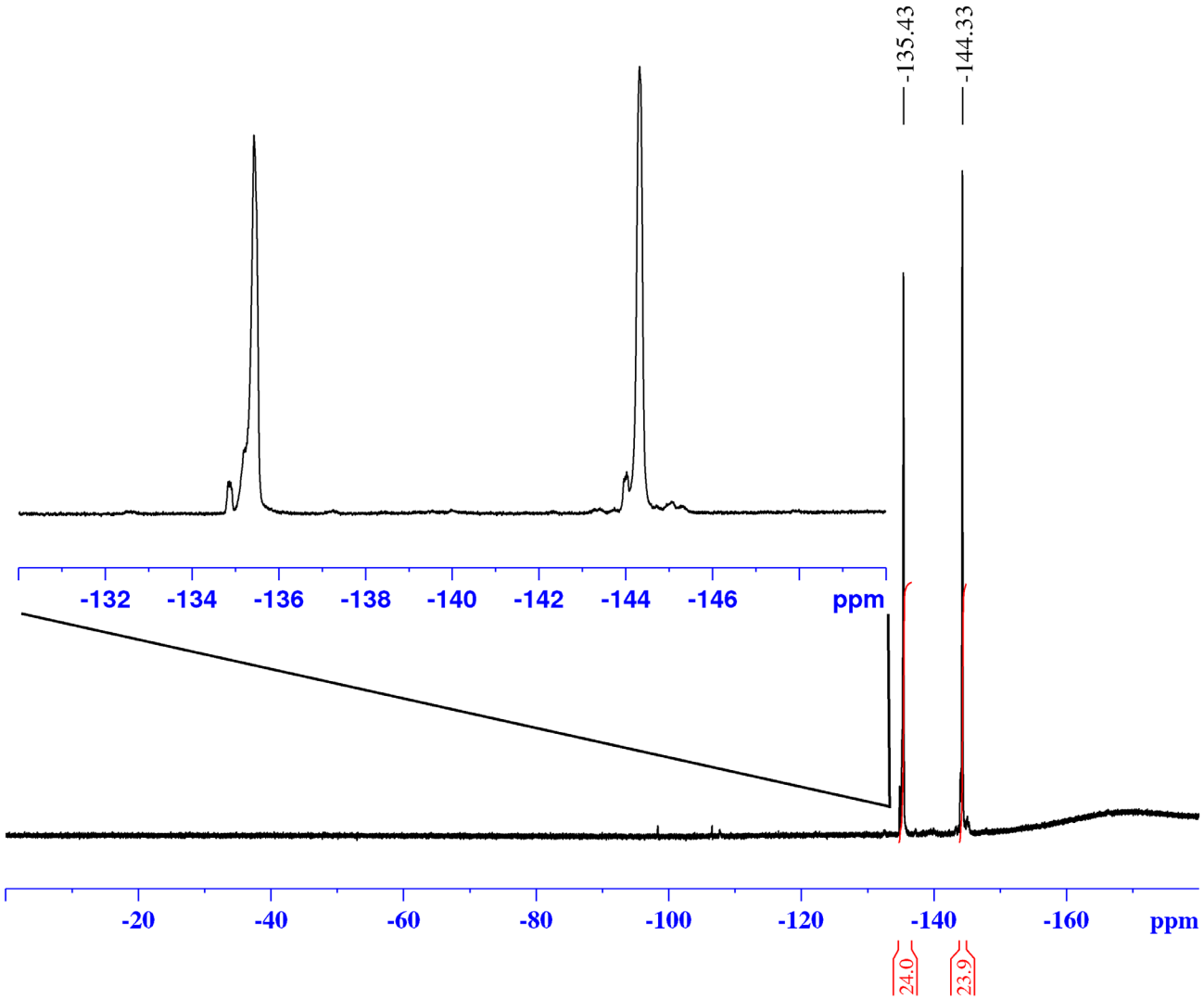
F2 - Acquisition Parameters
Date_ 20151209
Time 20.03
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

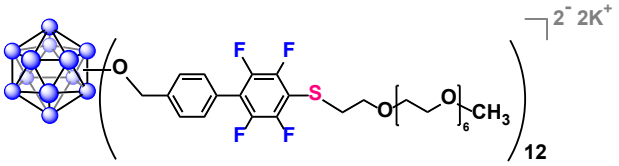


Current Data Parameters
NAME 1209
EXPNO 110
PROCNO 1

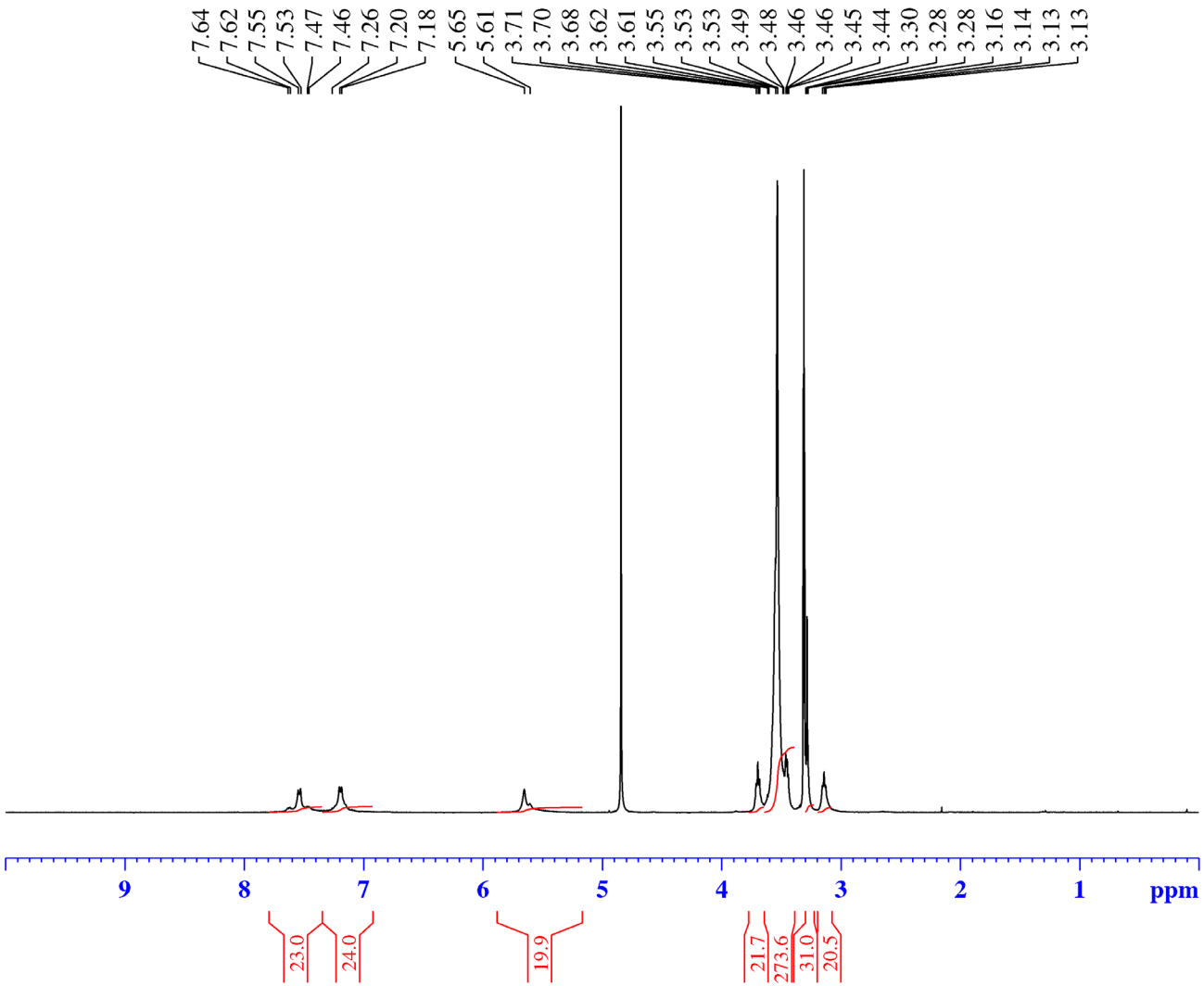
F2 - Acquisition Parameters
Date_ 20151209
Time 20.00
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

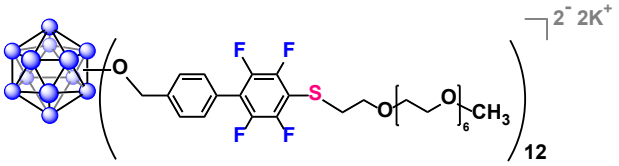


Current Data Parameters
NAME G2 PEG350 1217 1209 (MeOD)
EXPNO 2
PROCNO 1

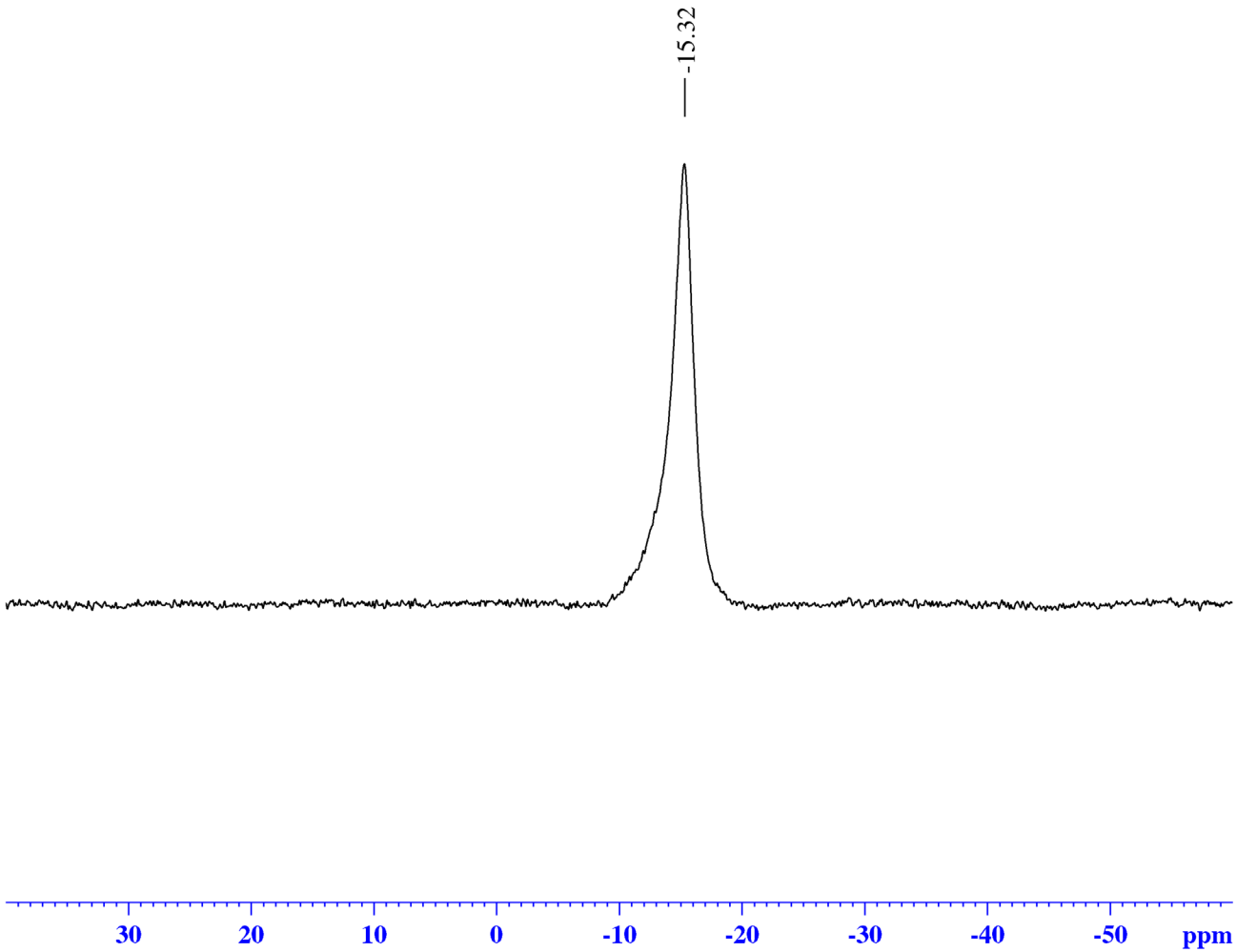
F2 - Acquisition Parameters
Date_ 20151220
Time 13.12
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

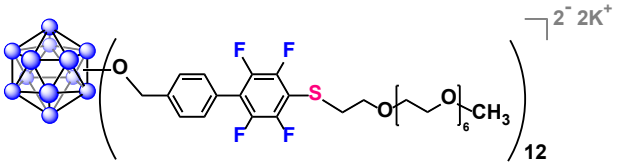


Current Data Parameters
NAME G2 PEG350 1217 1209 (MeOD)
EXPNO 3
PROCNO 1

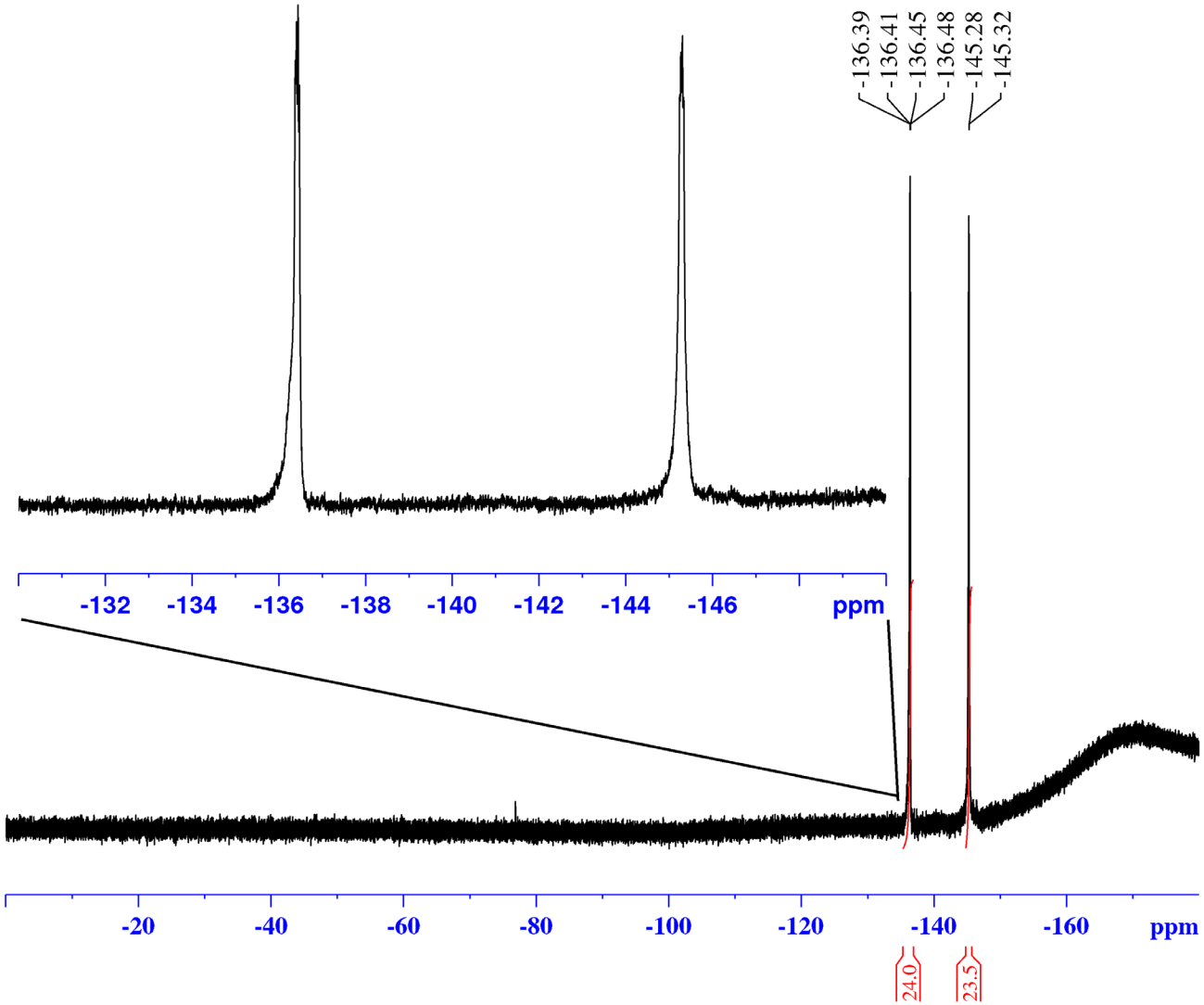
F2 - Acquisition Parameters
Date_ 20151220
Time 13.15
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

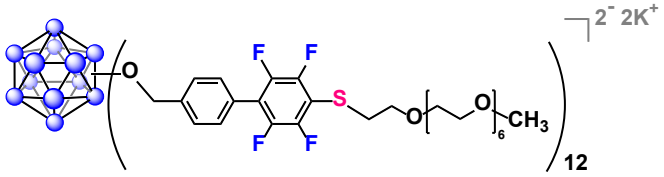


Current Data Parameters
NAME G2 PEG350 1217 1209 (MeOD)
EXPNO 4
PROCNO 1

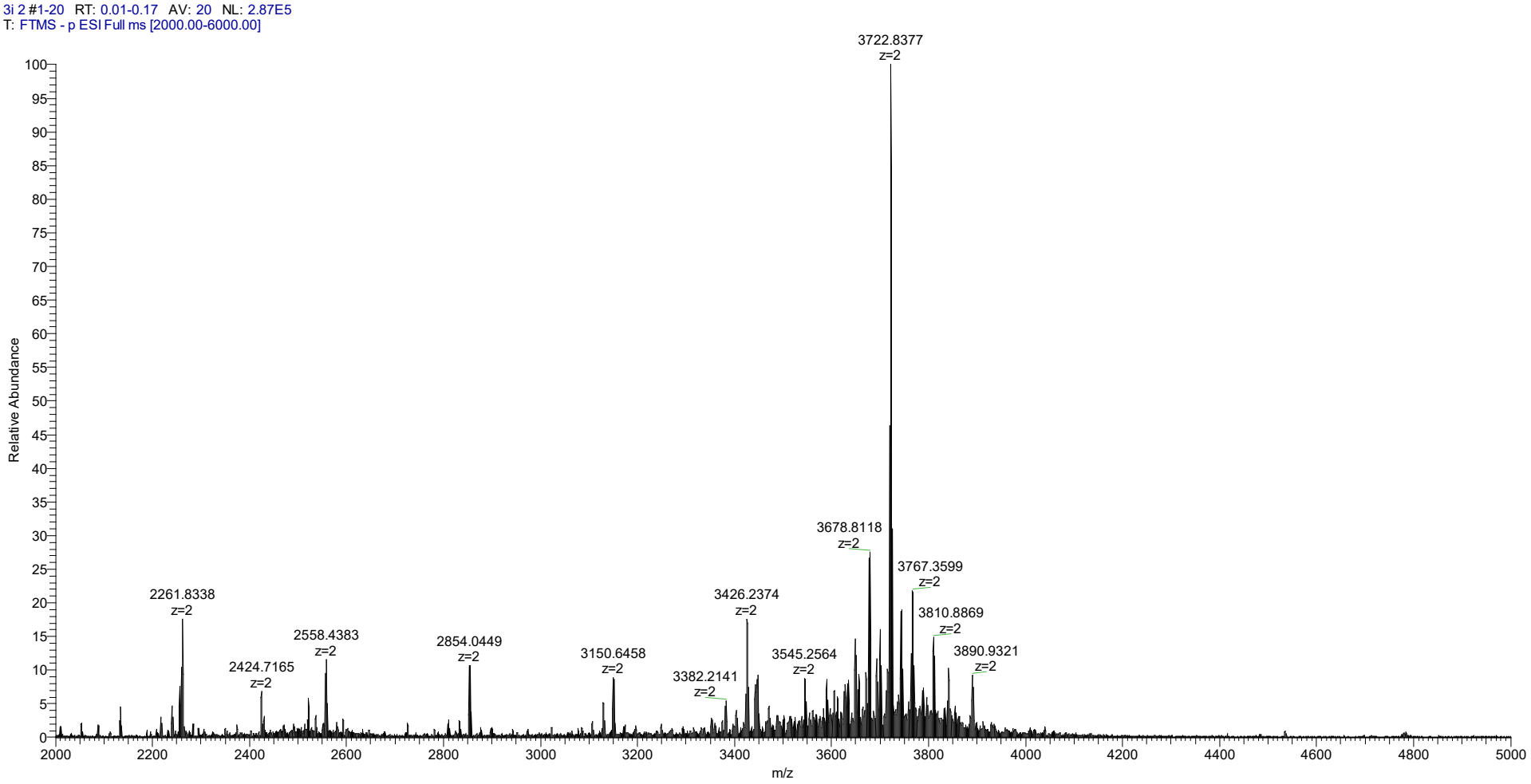
F2 - Acquisition Parameters
Date_ 20151220
Time 13.19
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

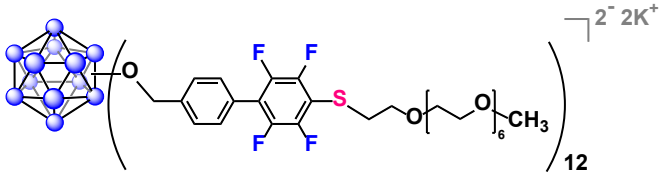
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

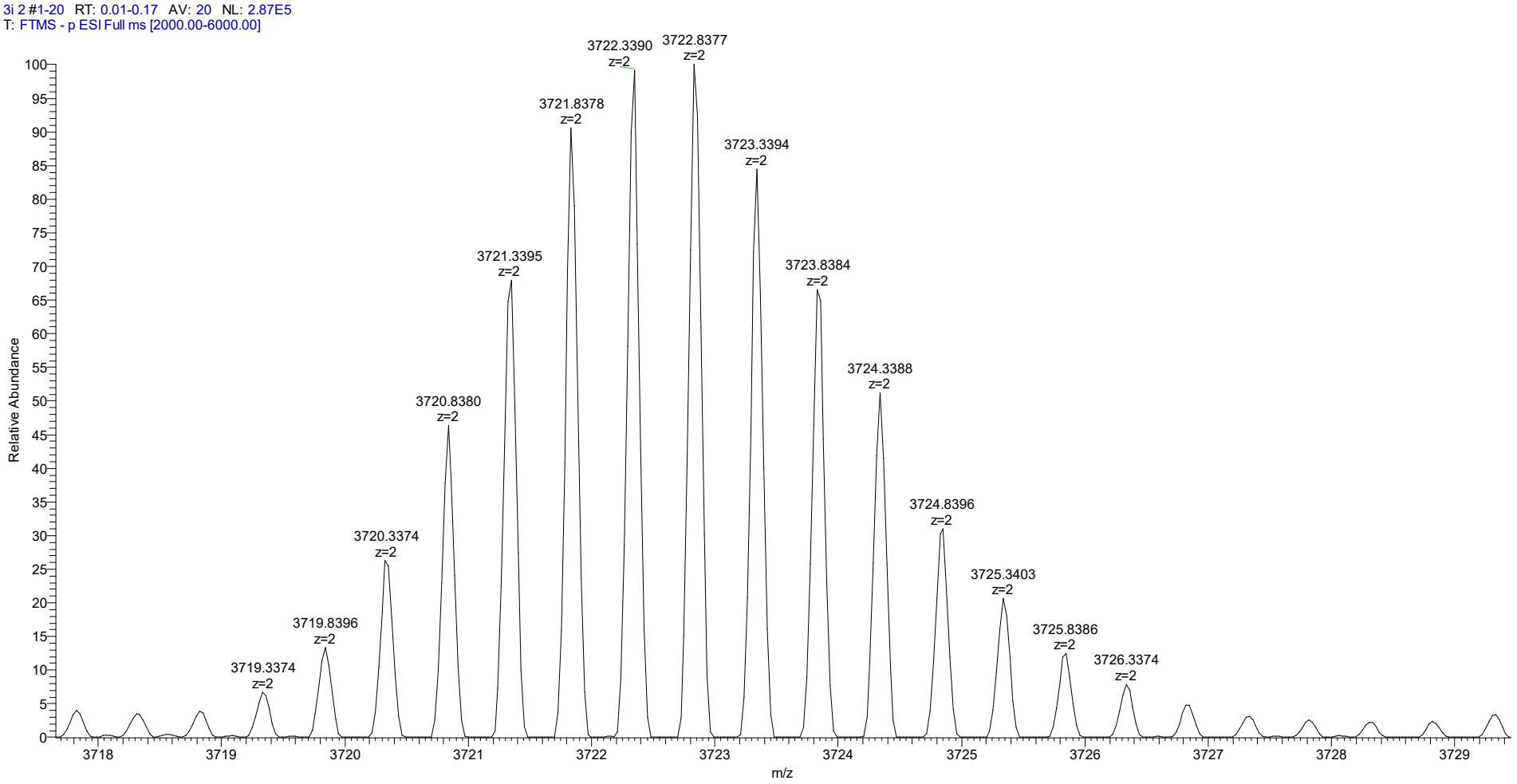


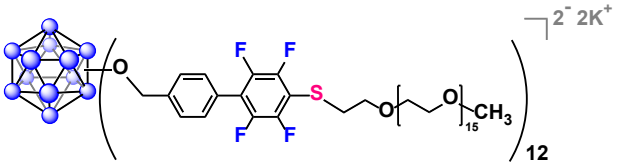
Q Exactive
High-Res Mass Spec



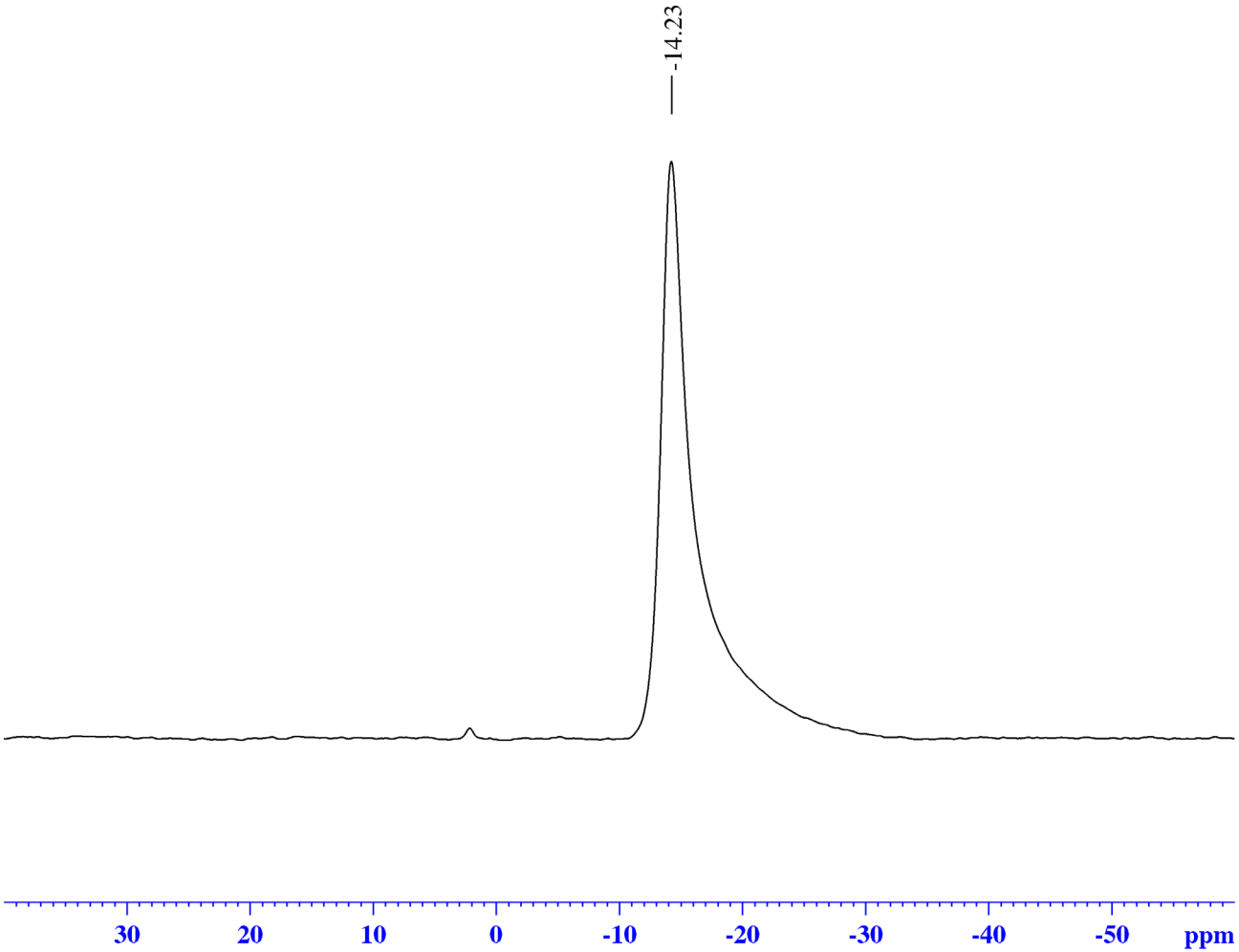


Q Exactive
High-Res Mass Spec





in situ ^{11}B NMR

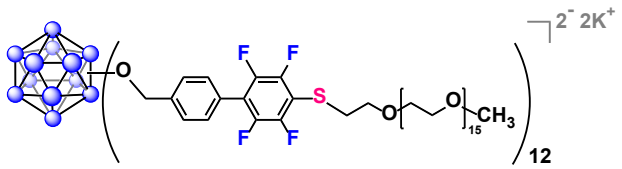


Current Data Parameters
NAME 0115
EXPNO 2
PROCNO 1

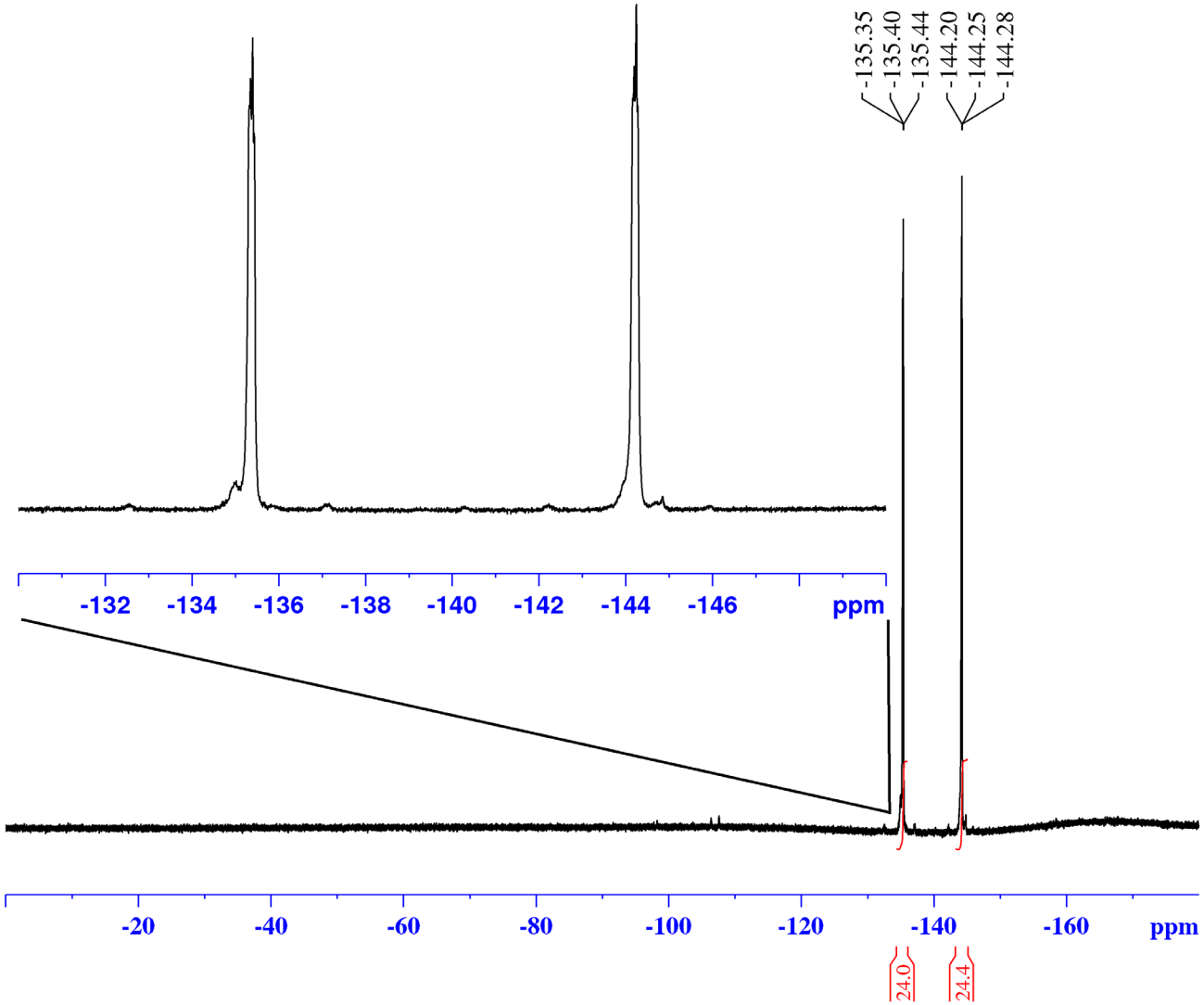
F2 - Acquisition Parameters
Date_ 20160115
Time 20.01
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 3848
SOLVENT C6D6
NS 1024
DS 0
SWH 38535.645 Hz
FIDRES 10.014461 Hz
AQ 0.0499278 sec
RG 114
DW 12.975 usec
DE 6.00 usec
TE 297.7 K
D1 0.00000400 sec
TD0 1

======== CHANNEL f1 ========
NUC1 11B
P1 5.00 usec
PL1 -2.00 dB
SFO1 96.2936310 MHz

F2 - Processing parameters
SI 32768
SF 96.2935644 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

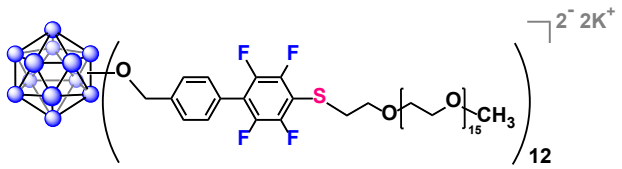


Current Data Parameters
NAME 0115
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160115
Time 19.55
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 131072
SOLVENT C6D6
NS 64
DS 0
SWH 75187.969 Hz
FIDRES 0.573639 Hz
AQ 0.8716288 sec
RG 2298.8
DW 6.650 usec
DE 6.00 usec
TE 297.7 K
D1 2.00000000 sec
TD0 1

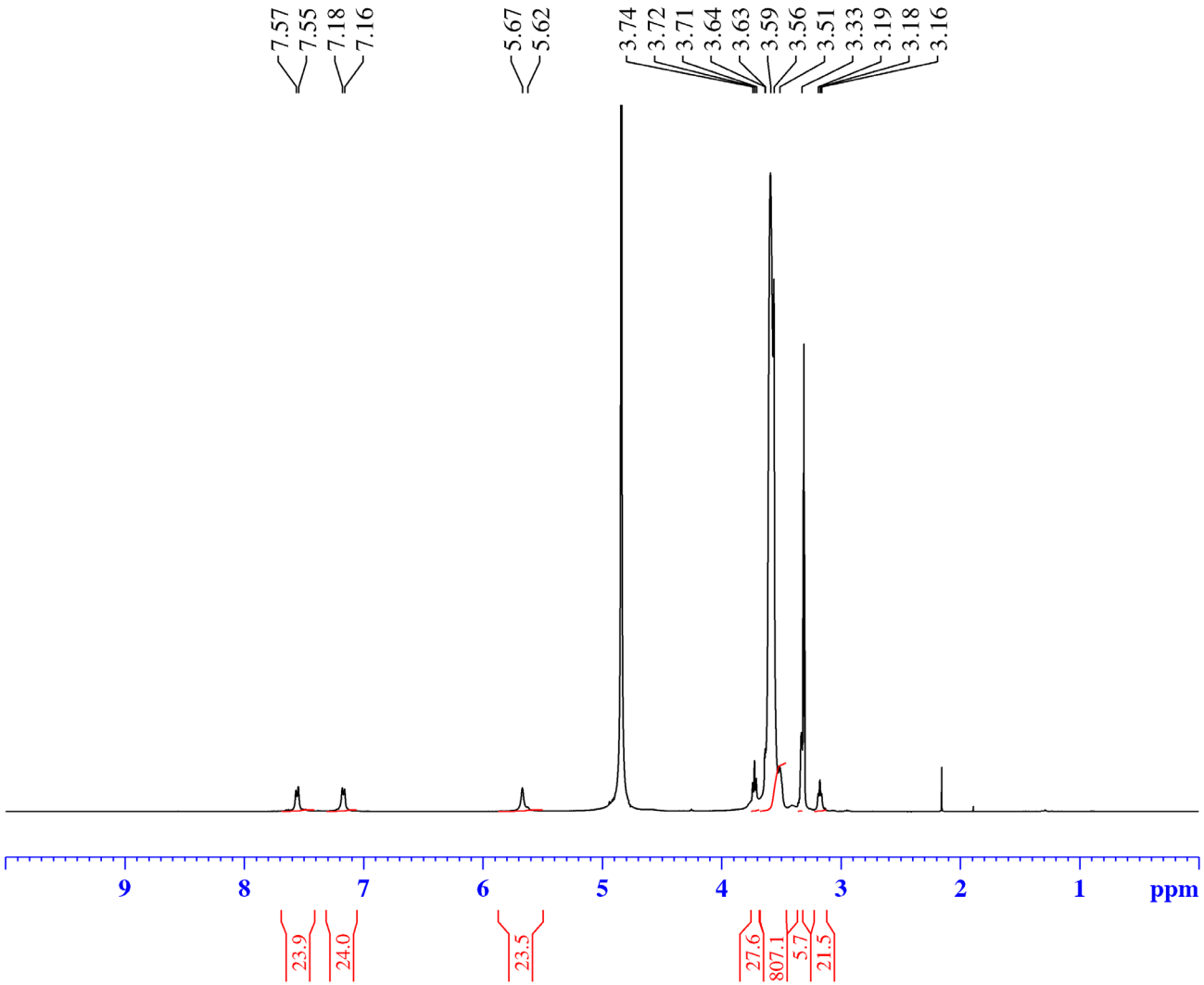
======== CHANNEL f1 ========
NUC1 19F
P1 13.75 usec
PL1 -2.00 dB
PL1W 19.90535927 W
SFO1 282.3761146 MHz

F2 - Processing parameters
SI 65536
SF 282.4043550 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{1}H NMR

BRUKER

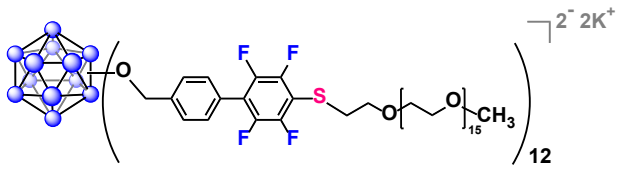


Current Data Parameters
NAME G2 PEG750 (MeOD)
EXPNO 160
PROCNO 1

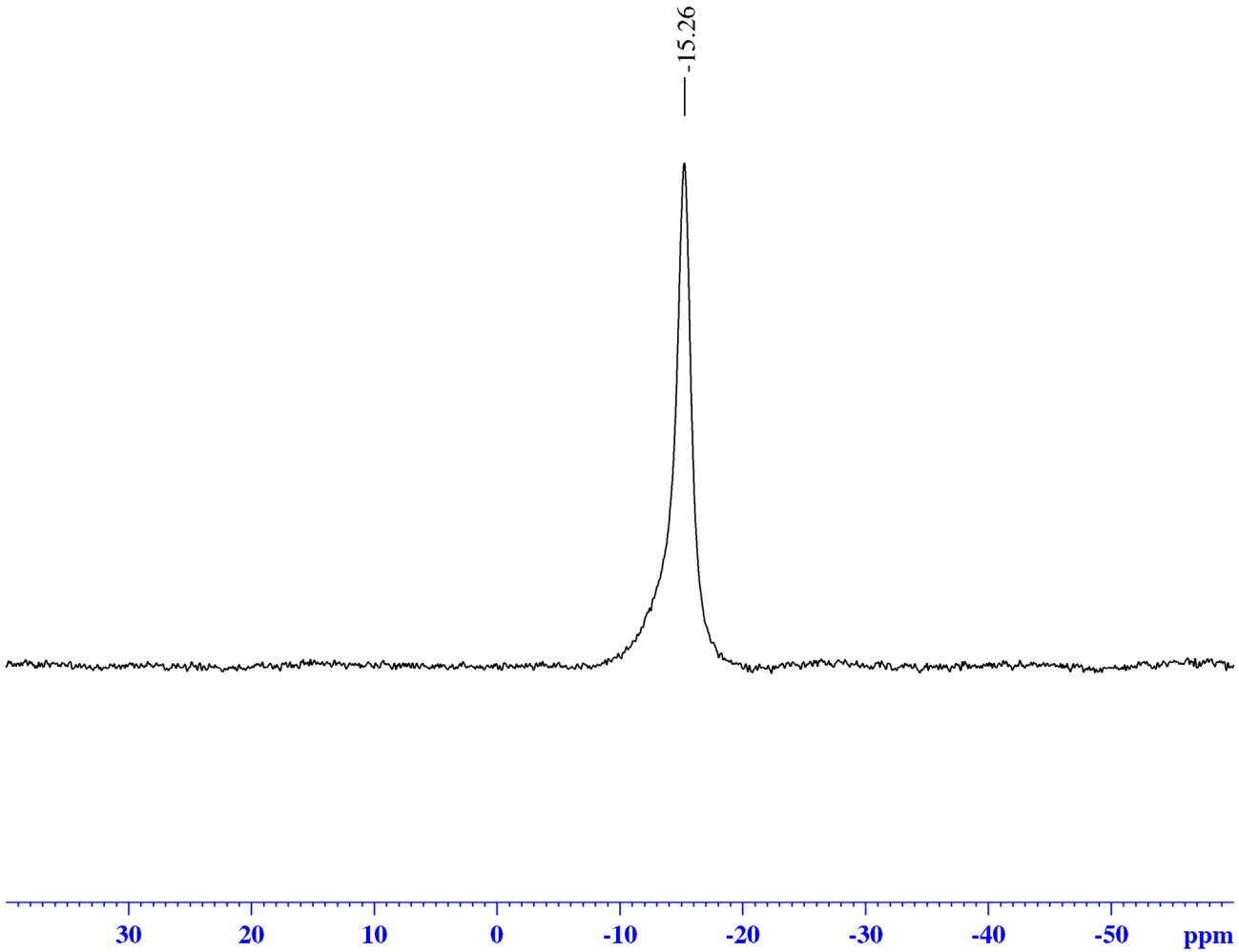
F2 - Acquisition Parameters
Date_ 20160119
Time 20.06
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 83.63
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 4.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300080 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR

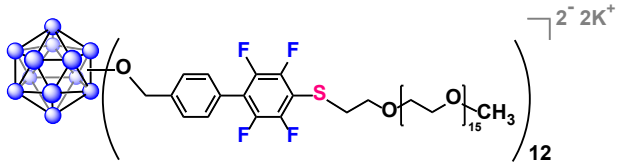


Current Data Parameters
NAME G2 PEG750 (MeOD)
EXPNO 161
PROCNO 1

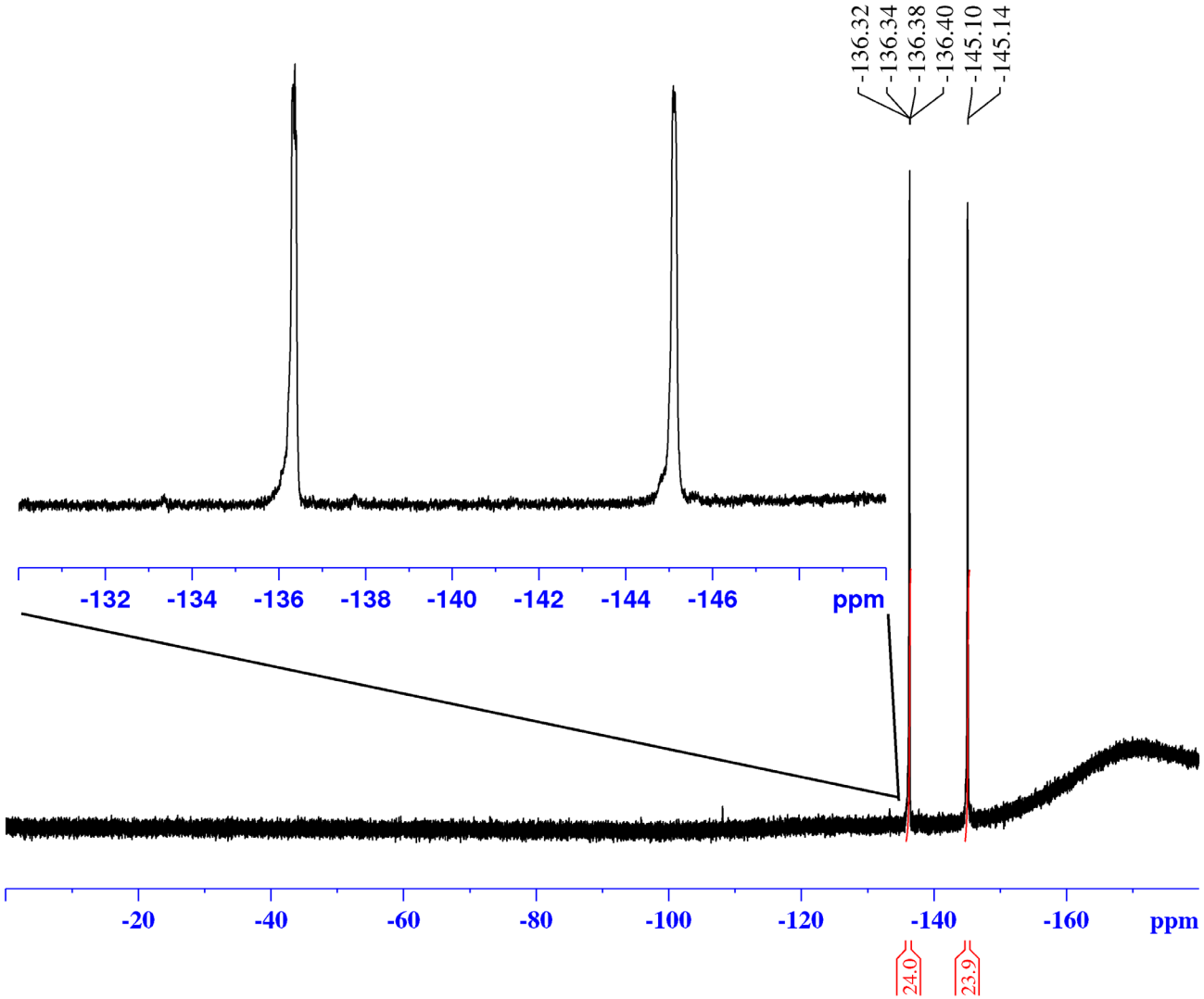
F2 - Acquisition Parameters
Date_ 20160119
Time 20.09
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



^{19}F NMR

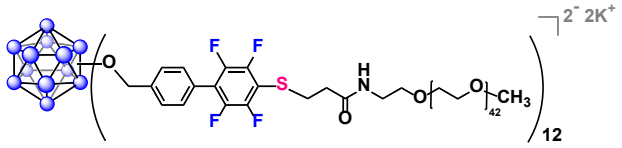


Current Data Parameters
NAME G2 PEG750 (MeOD)
EXPNO 162
PROCNO 1

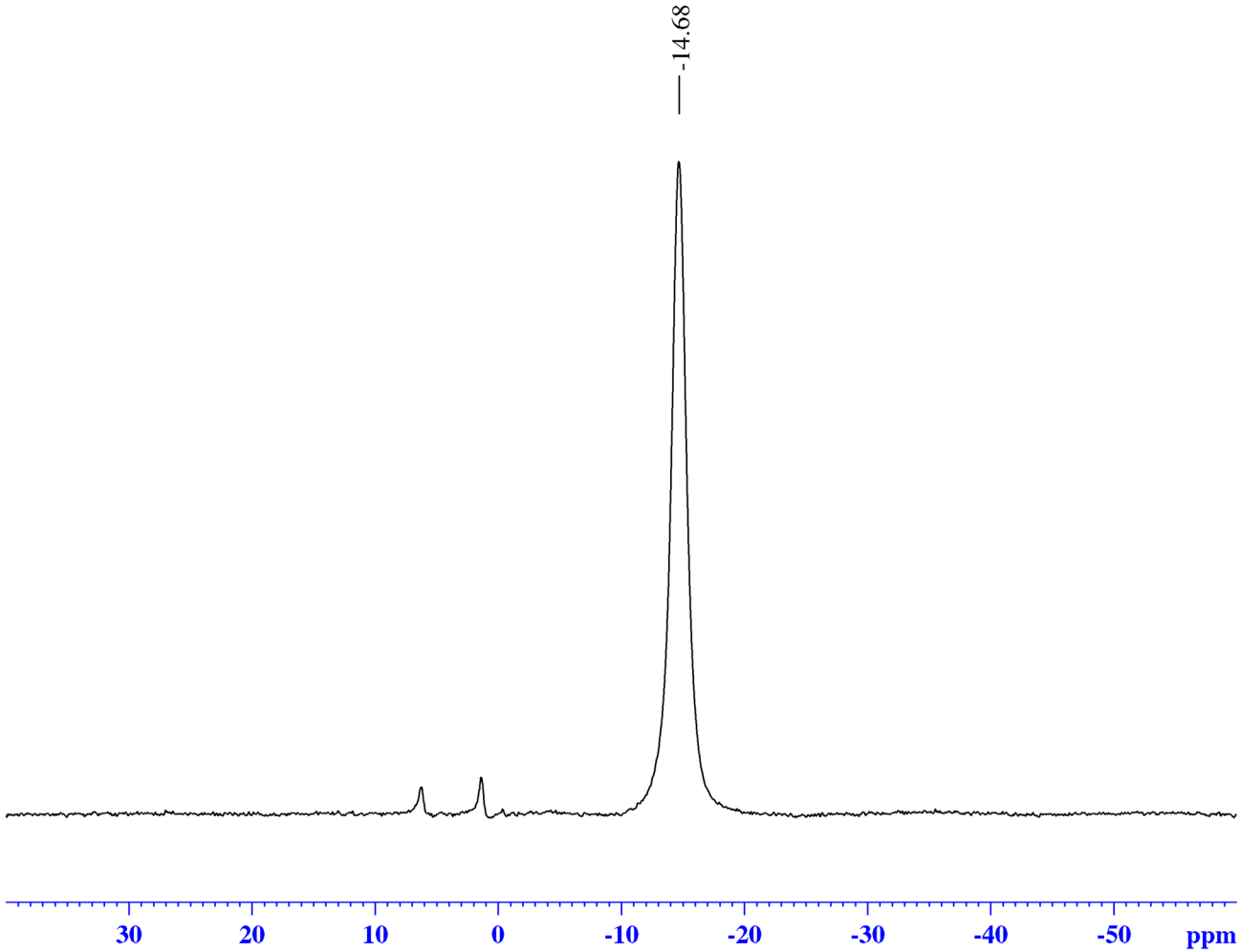
F2 - Acquisition Parameters
Date_ 20160119
Time 20.13
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



in situ ^{11}B NMR

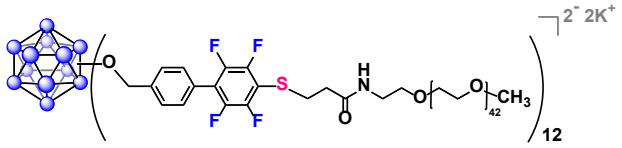


Current Data Parameters
NAME 0126
EXPNO 81
PROCNO 1

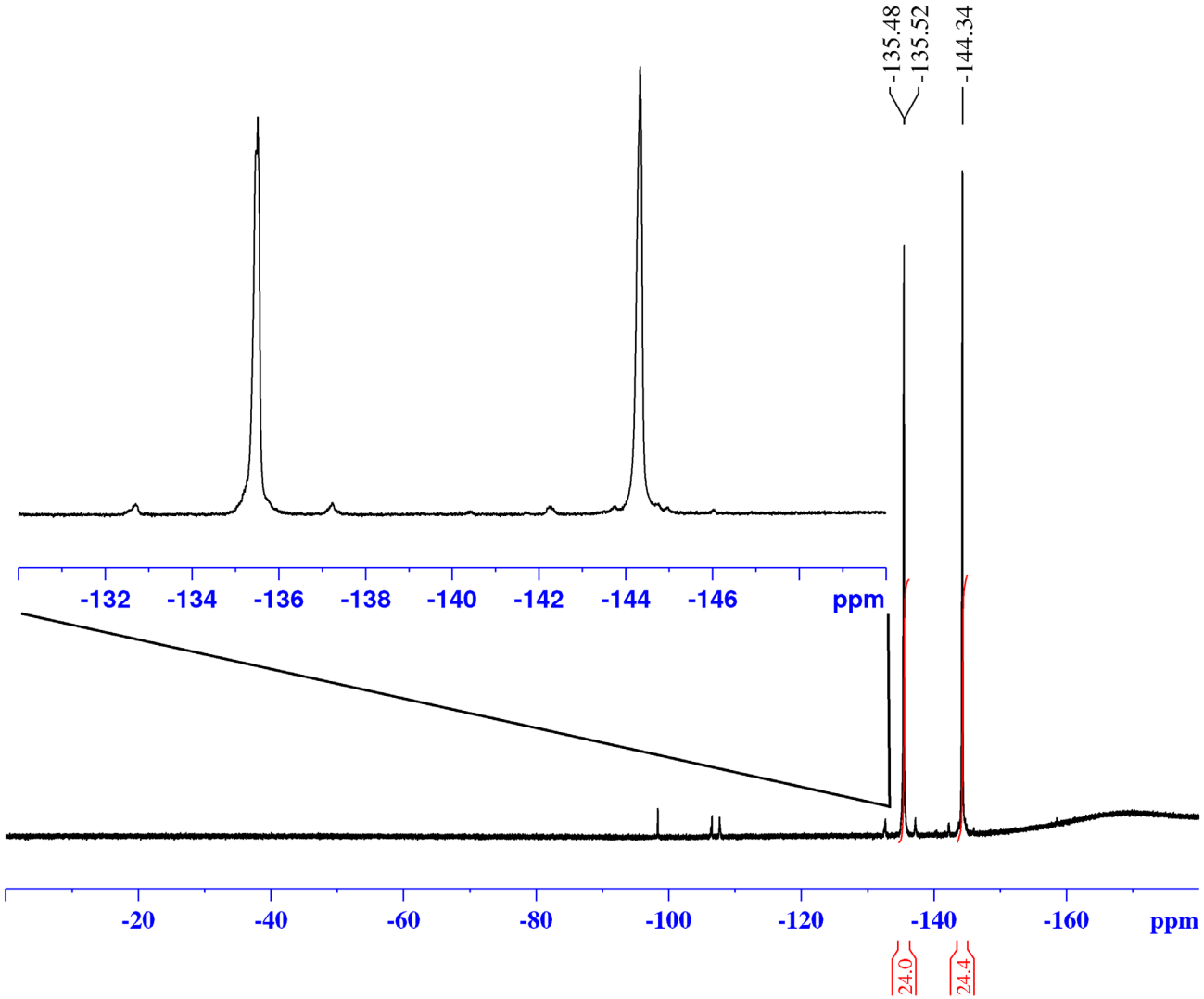
F2 - Acquisition Parameters
Date_ 20160126
Time 16.30
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



in situ ^{19}F NMR

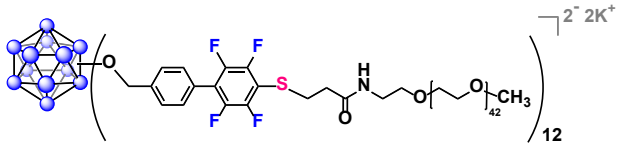


Current Data Parameters
NAME 0126
EXPNO 80
PROCNO 1

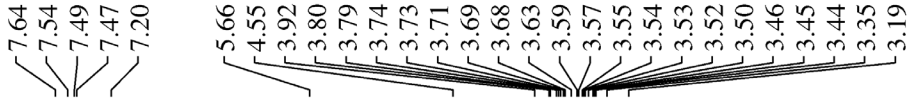
F2 - Acquisition Parameters
Date_ 20160126
Time 16.27
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

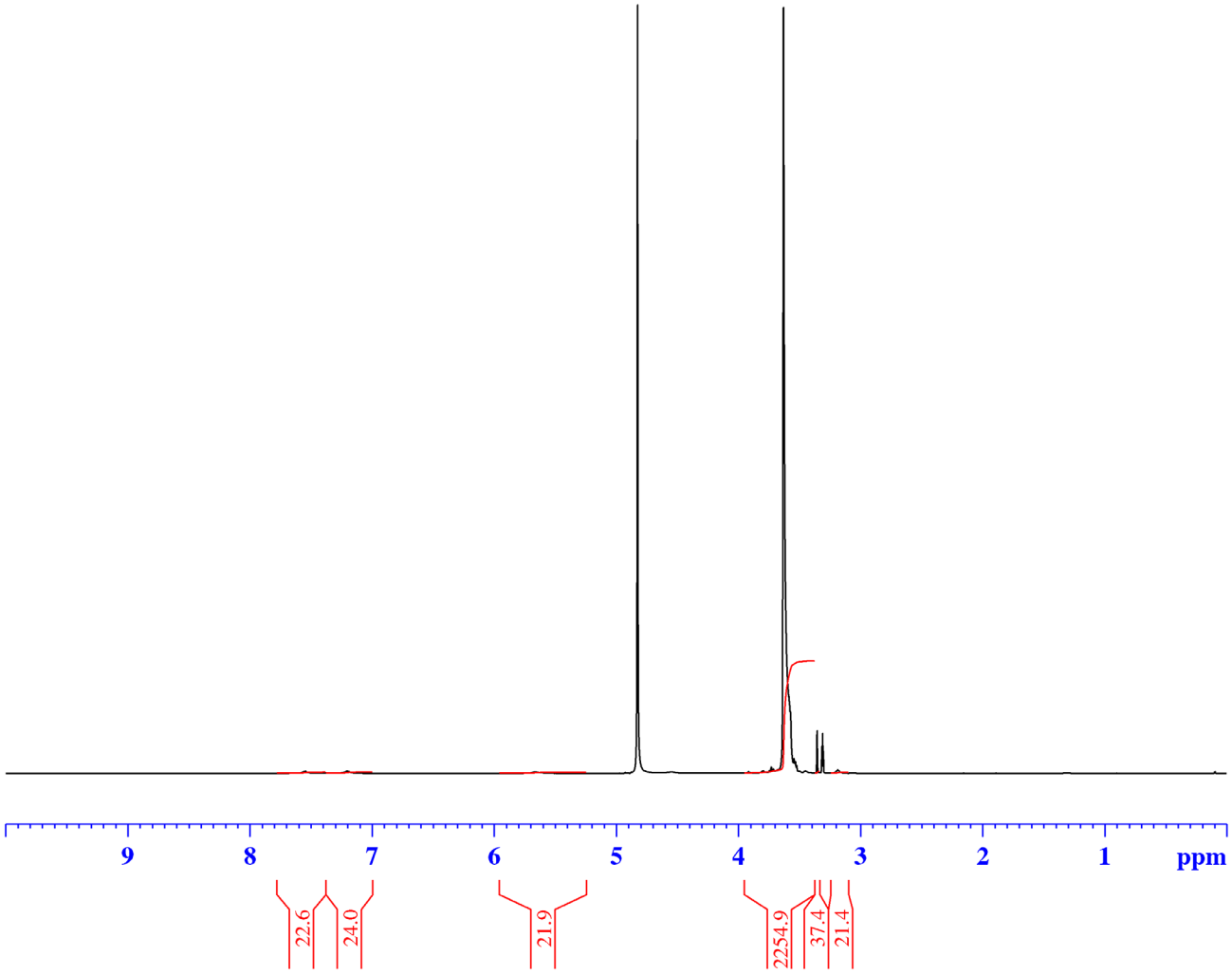
======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR



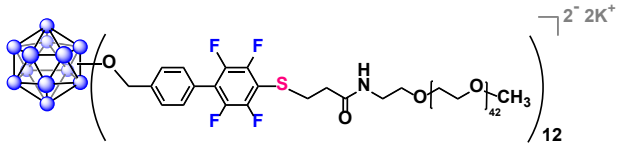


Current Data Parameters
NAME G2 PEG2000 0203 0125 MeOD
EXPNO 12
PROCNO 1

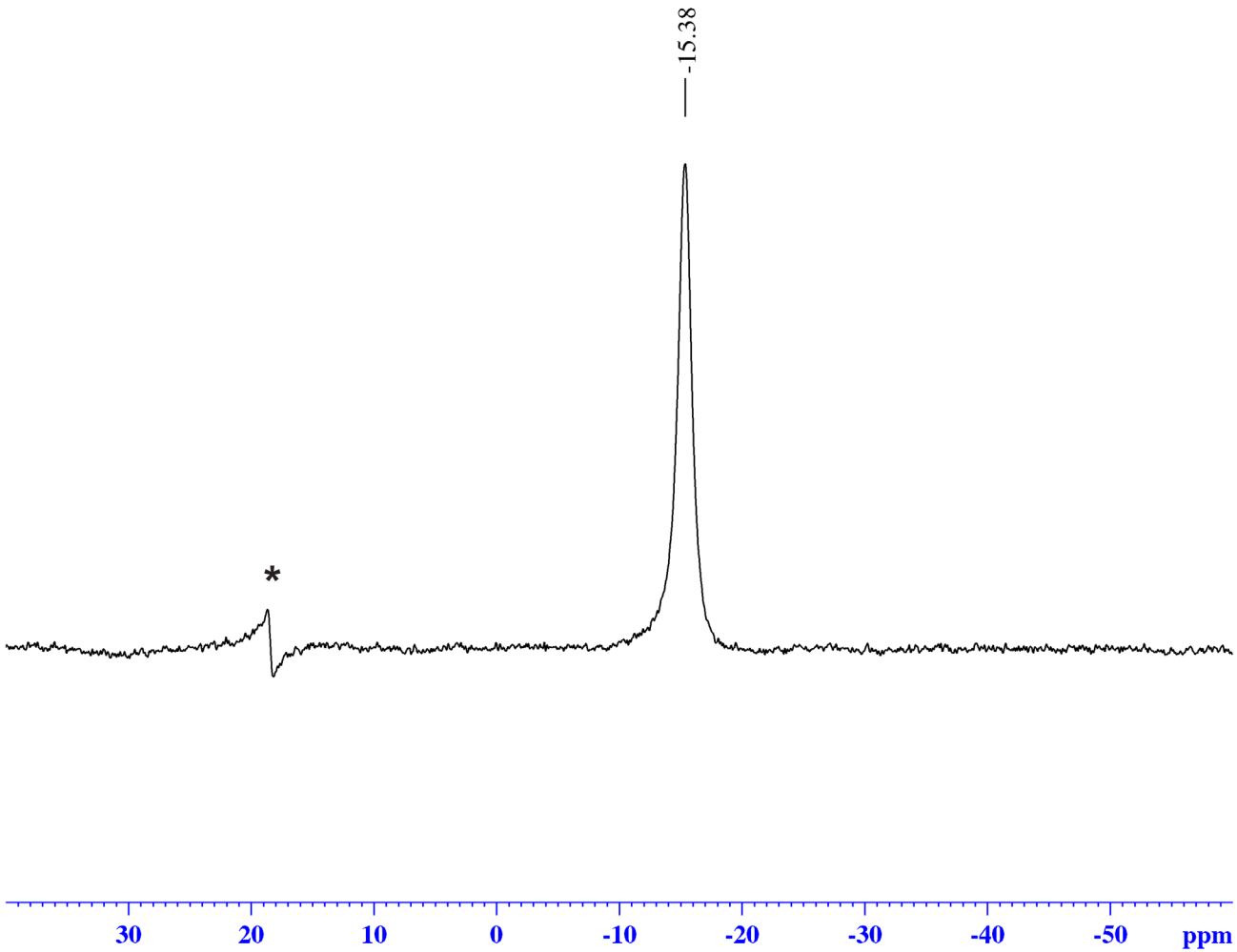
F2 - Acquisition Parameters
Date_ 20160204
Time 17.21
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 48.1
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{11}B NMR



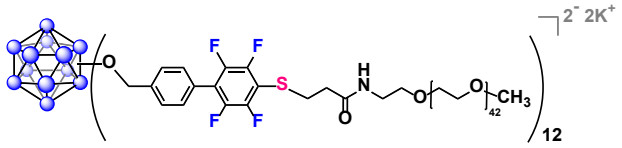
Current Data Parameters
NAME G2 PEG2000 0203 0125 MeOD
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160204
Time 17.11
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1

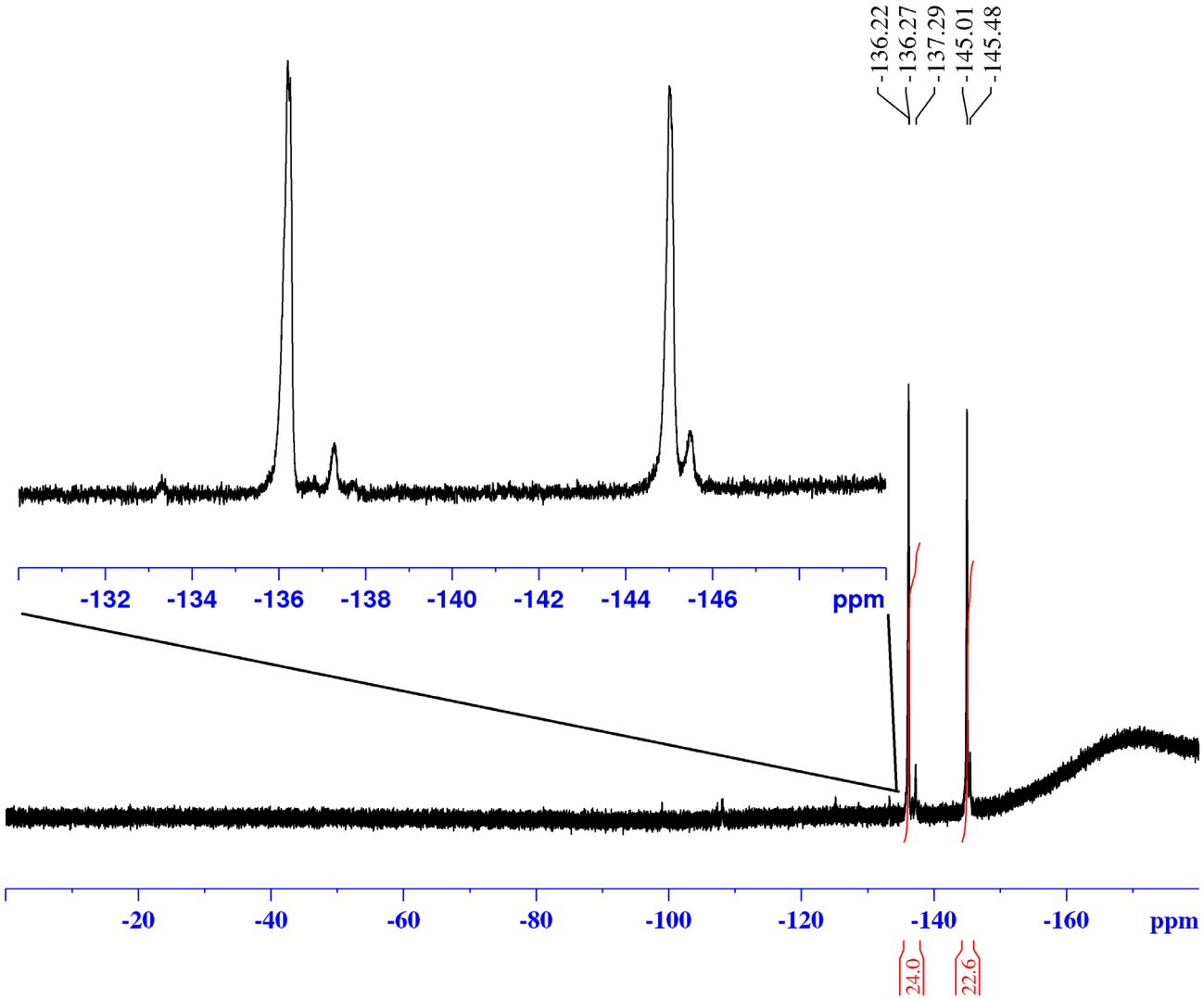
======== CHANNEL f1 ========
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

* This peak corresponds to a small boric acid impurity.



^{19}F NMR

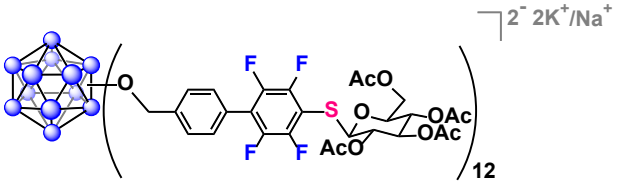


Current Data Parameters
NAME G2 PEG2000 0203 0125 MeOD
EXPNO 11
PROCNO 1

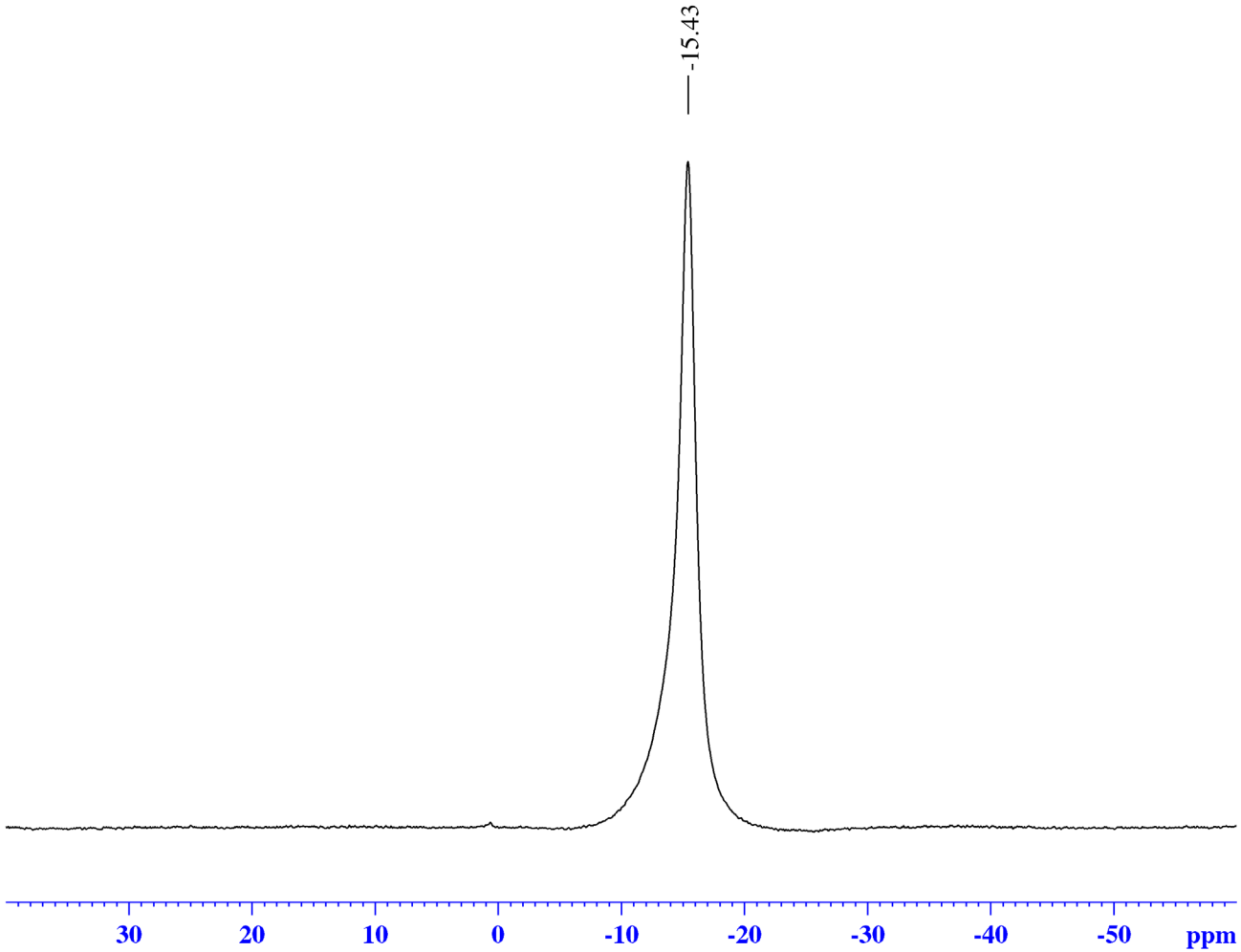
F2 - Acquisition Parameters
Date_ 20160204
Time 17.15
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



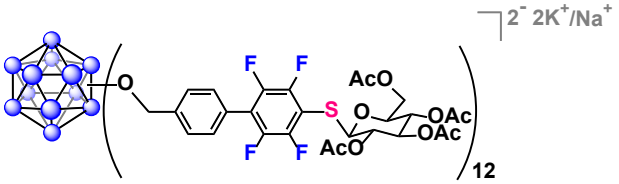
in situ ^{11}B NMR



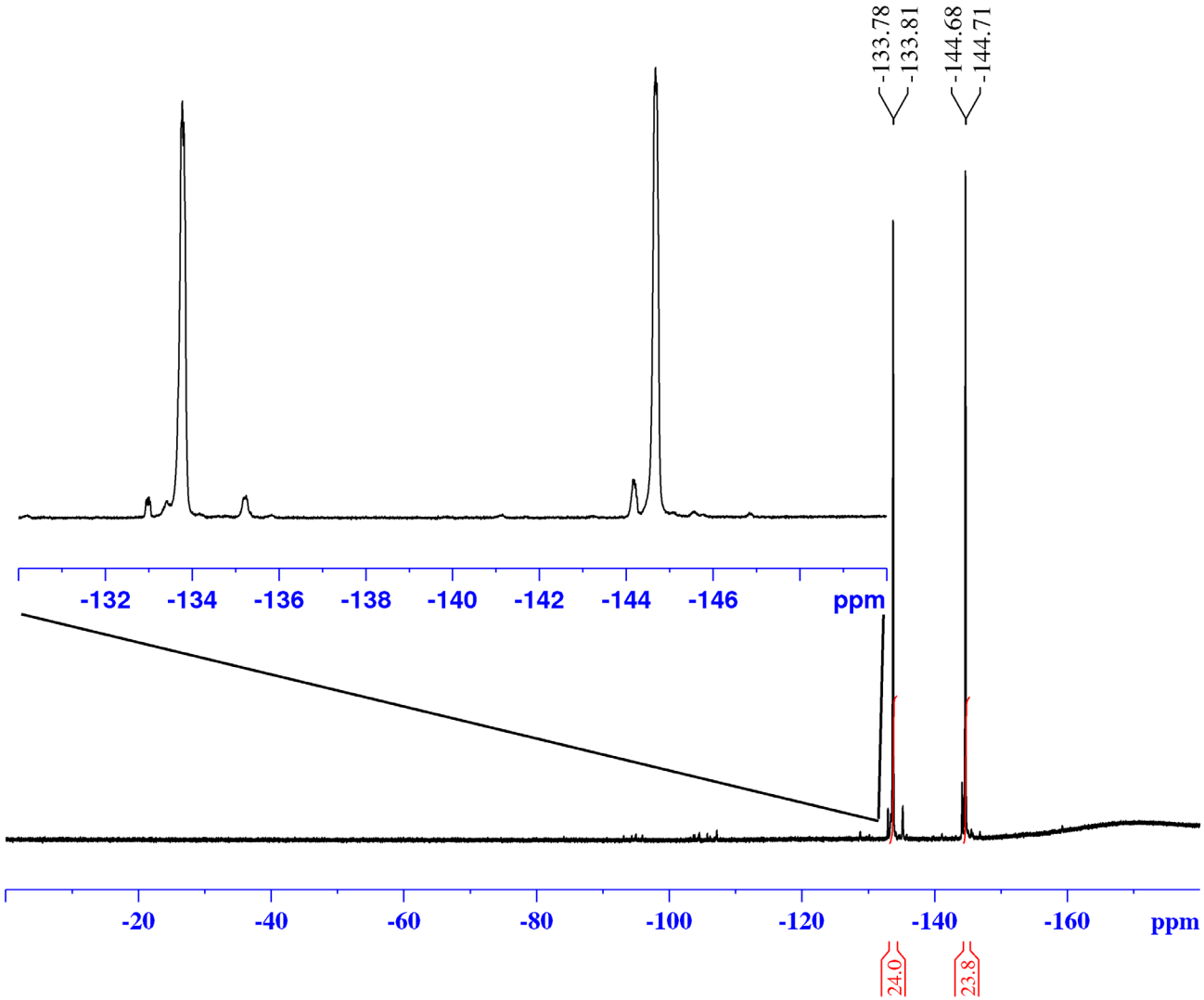
Current Data Parameters
NAME 0303
EXPNO 91
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160303
Time 20.25 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



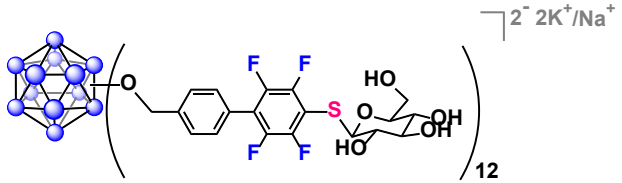
in situ ^{19}F NMR



Current Data Parameters
NAME 0303
EXPNO 90
PROCNO 1

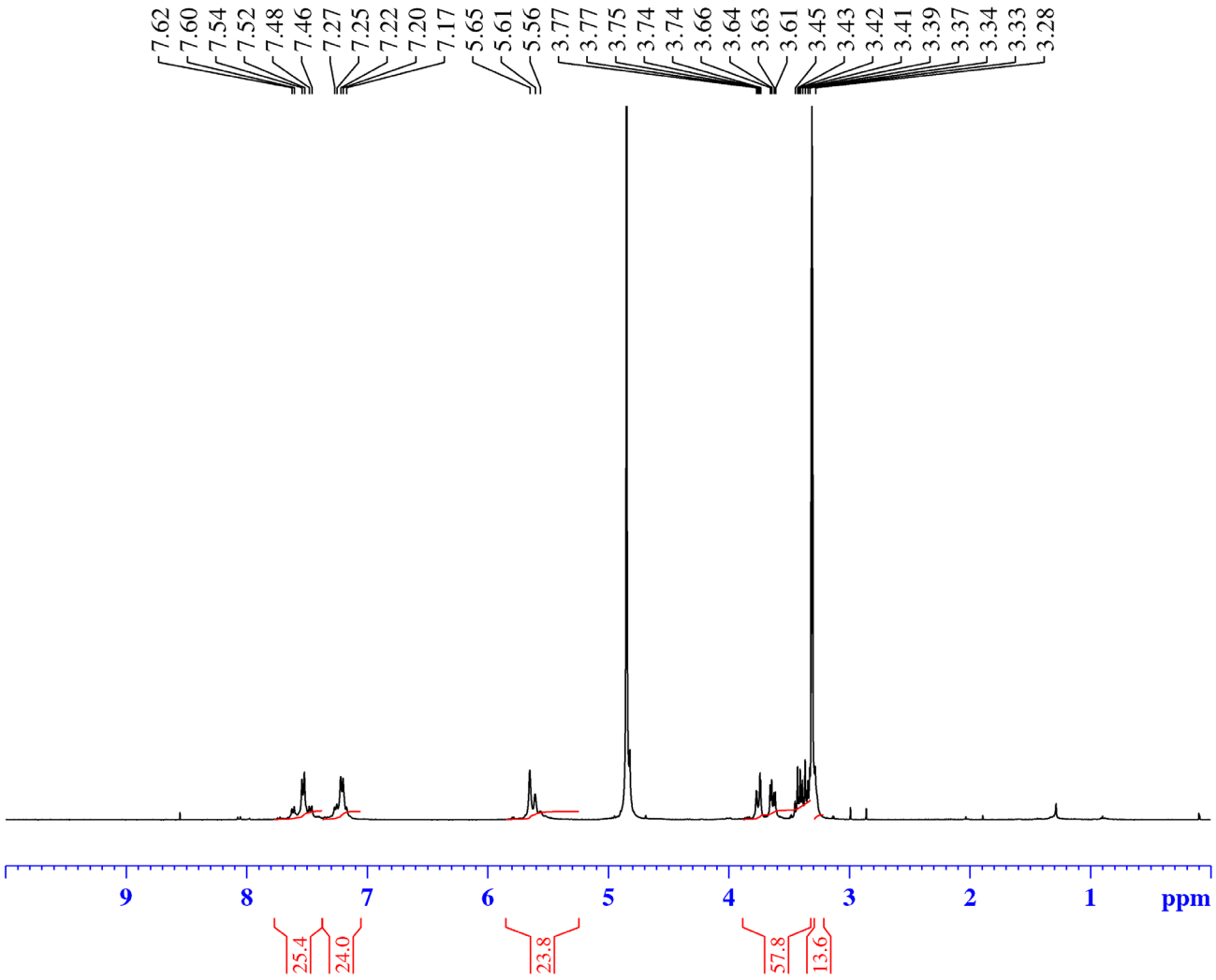
F2 - Acquisition Parameters
Date_ 20160303
Time 20.20 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zgflqn30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 1.144409 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

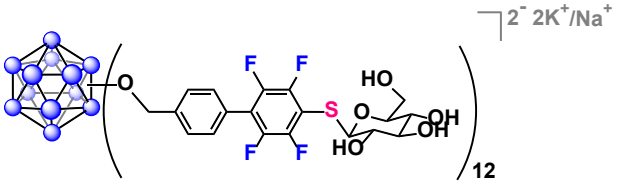
BRUKER



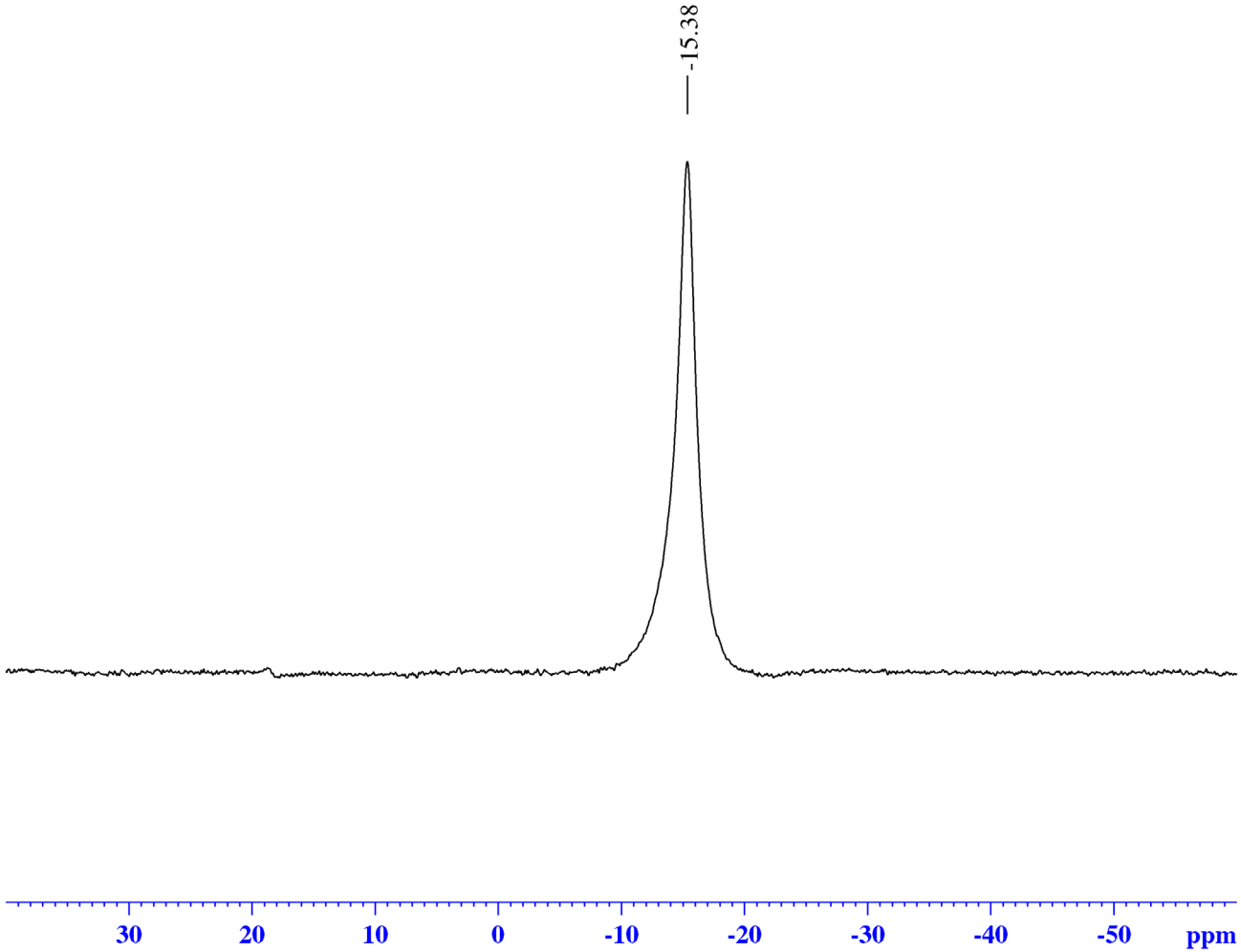
Current Data Parameters
NAME G2 Glc 0307 0303 (MeOD)
EXPNO 82
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160308
Time 15.59 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.303045 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



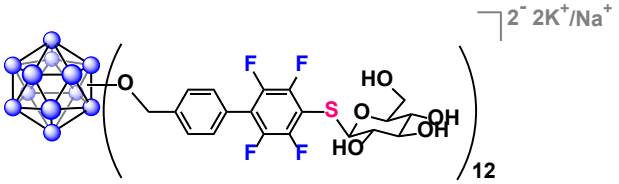
^{11}B NMR



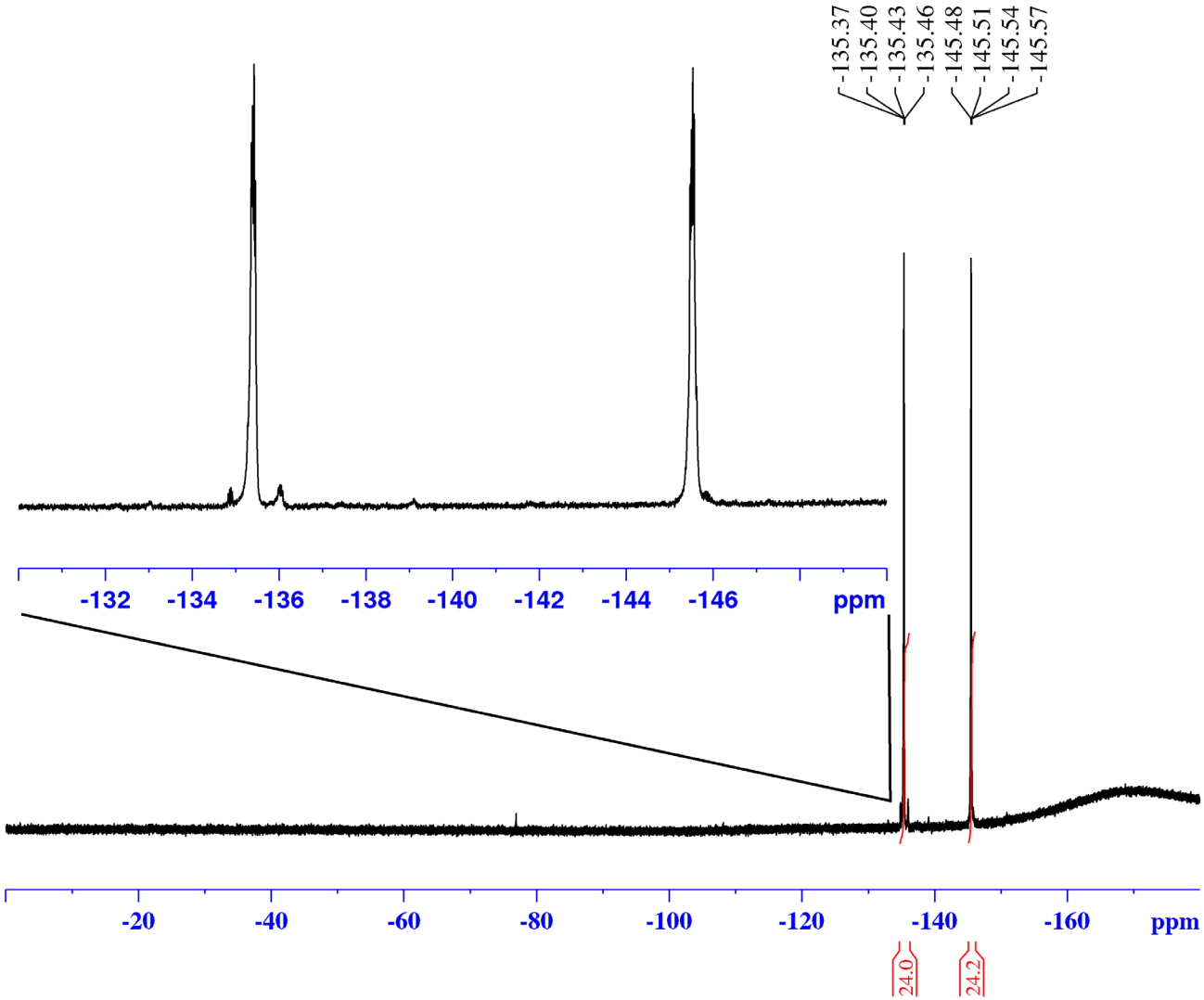
Current Data Parameters
NAME G2 Glc 0307 0303 (MeOD)
EXPNO 81
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160308
Time 15.54 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zg
TD 5096
SOLVENT MeOD
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 299.0 K
D1 0.05000000 sec
TD0 1
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



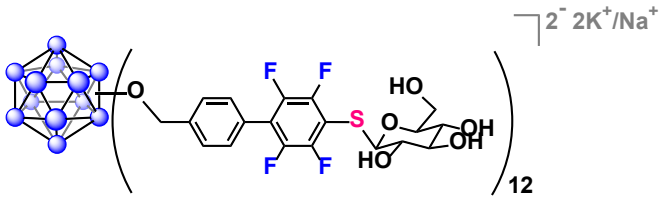
^{19}F NMR



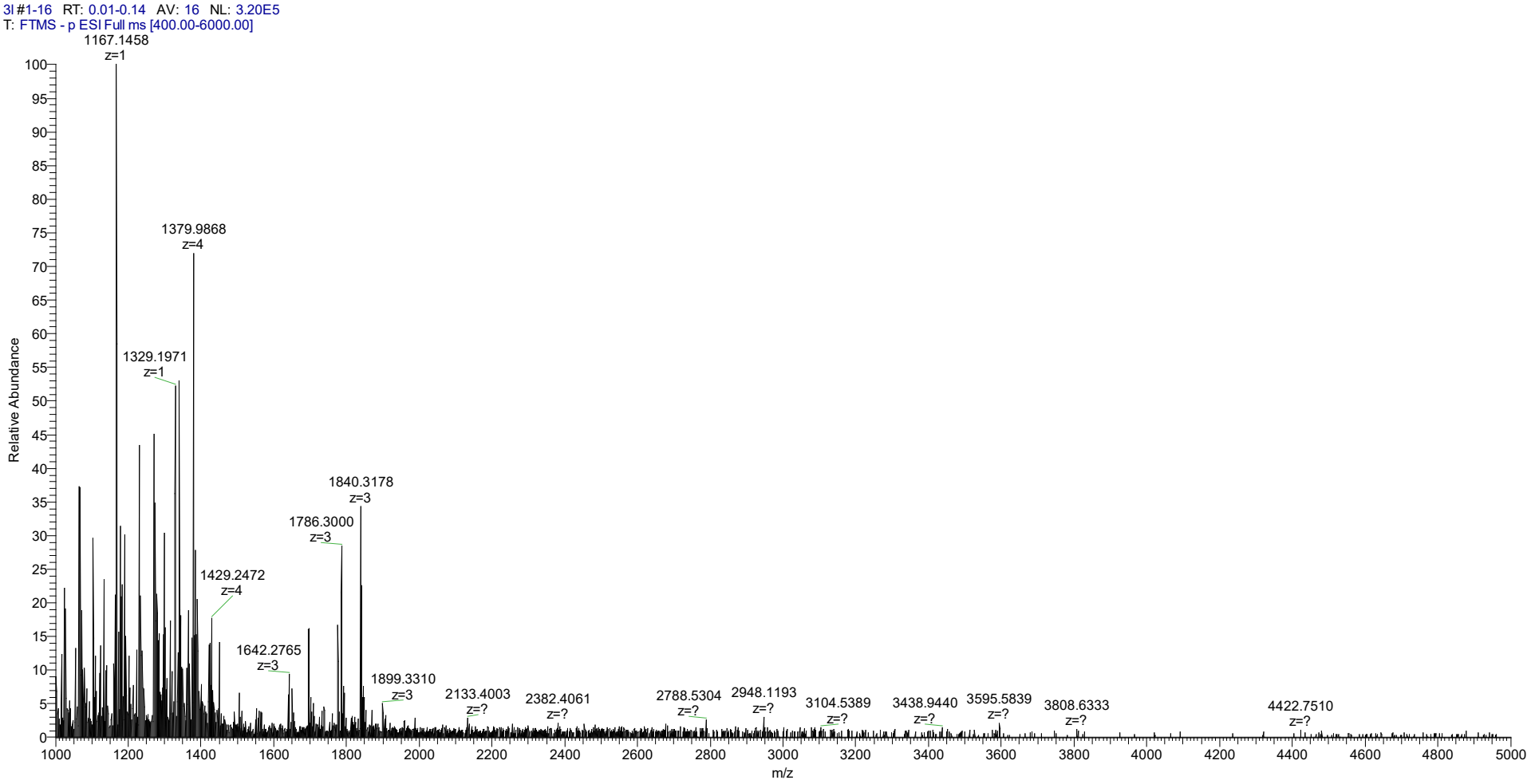
Current Data Parameters
NAME G2 Glc 0307 0303 (MeOD)
EXPNO 80
PROCNO 1

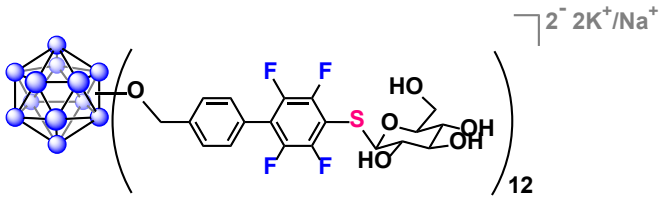
F2 - Acquisition Parameters
Date_ 20160308
Time 15.51 h
INSTRUM av400
PROBHD Z108618_0656 (
PULPROG zgflqn30
TD 262144
SOLVENT MeOD
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 1.144409 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

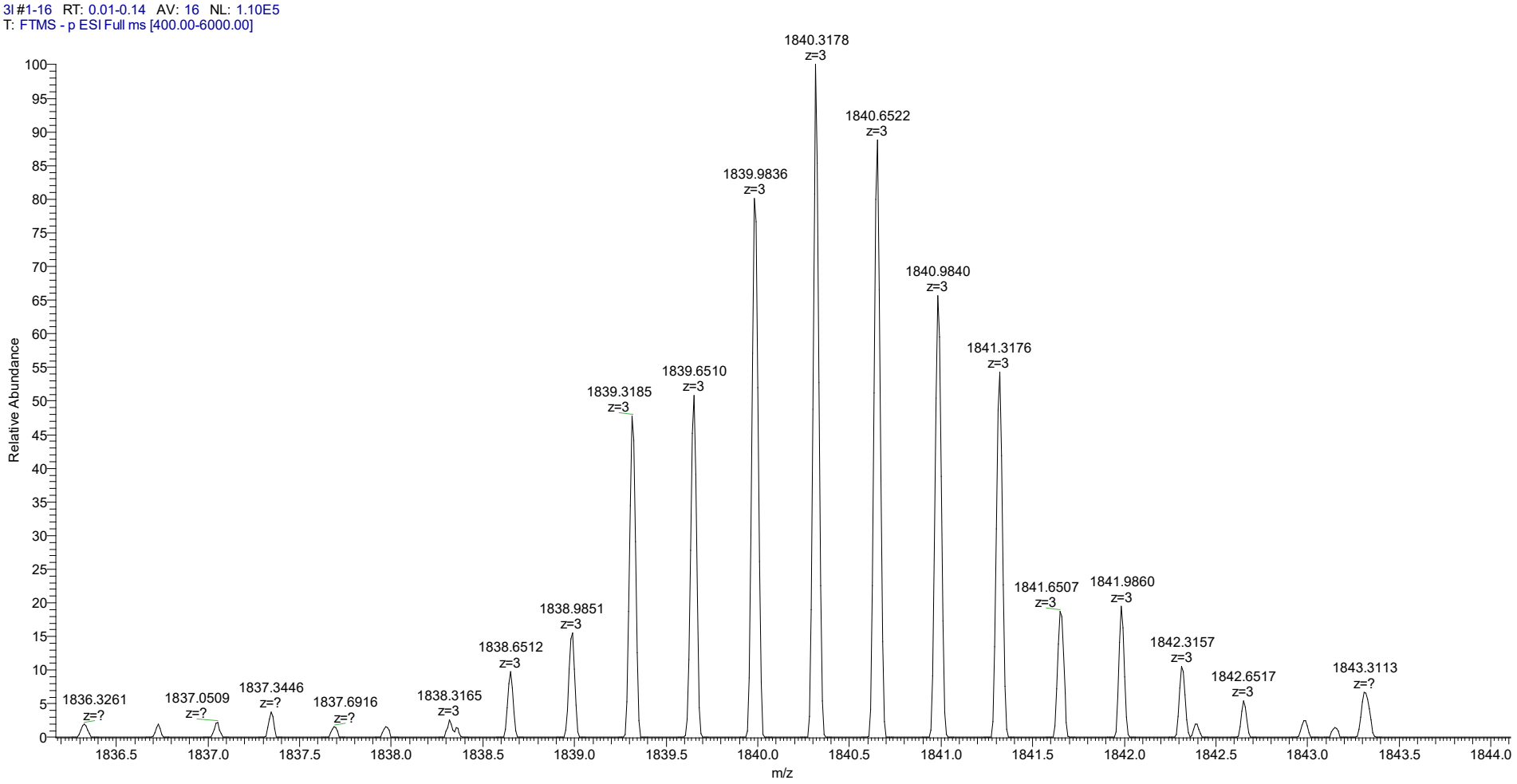


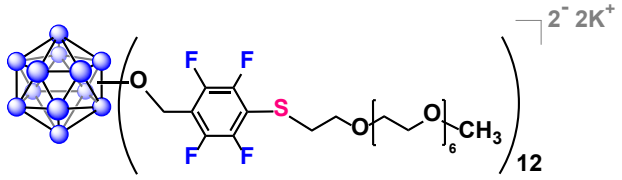
Q Exactive
High-Res Mass Spec



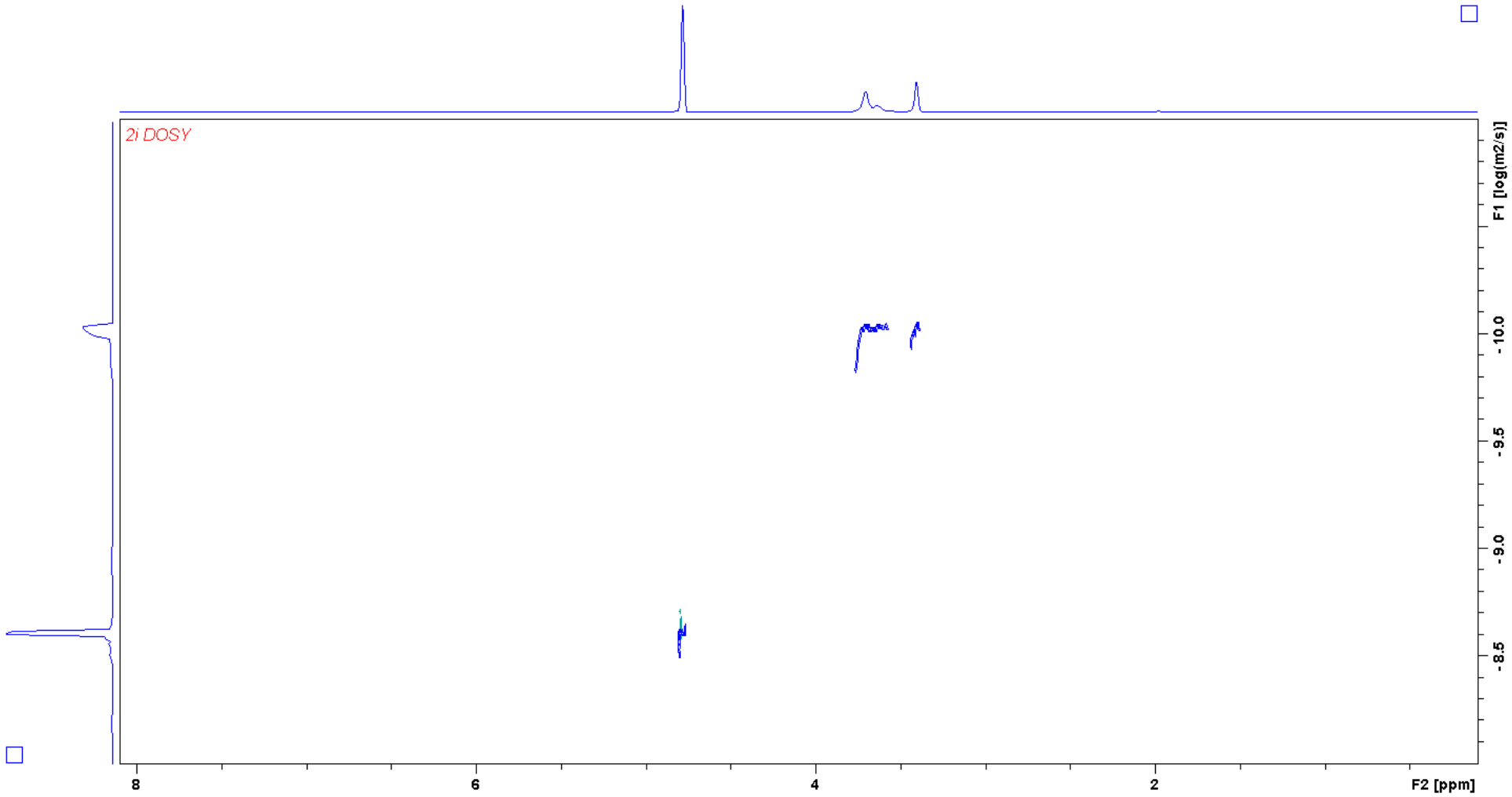


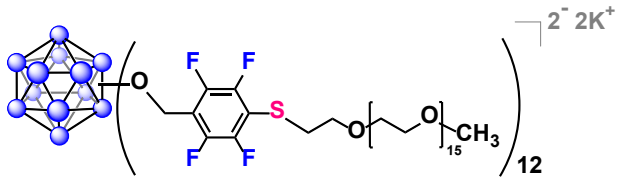
Q Exactive
High-Res Mass Spec





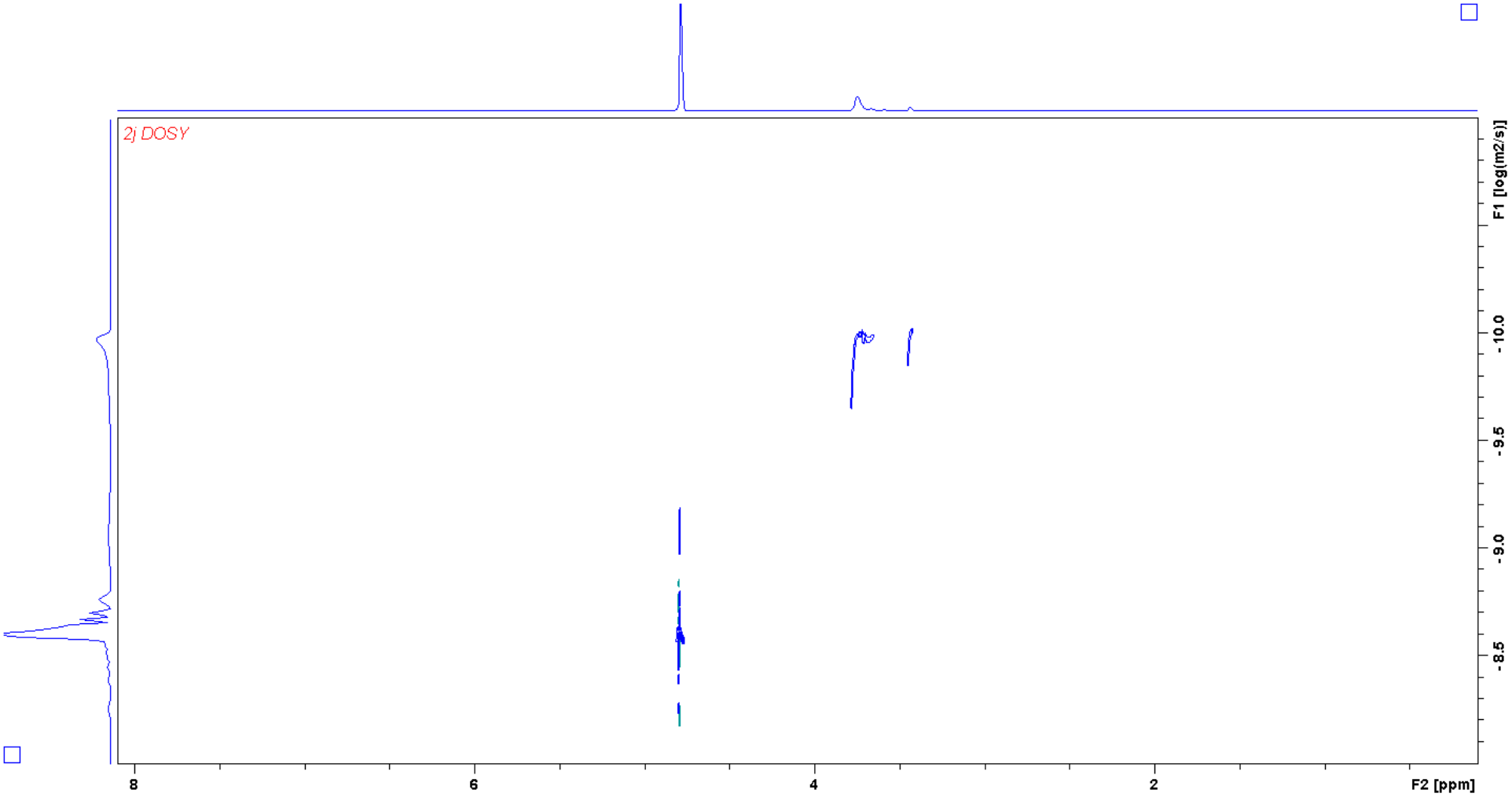
2D DOSY ^{1}H NMR

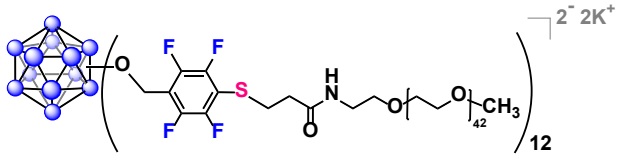




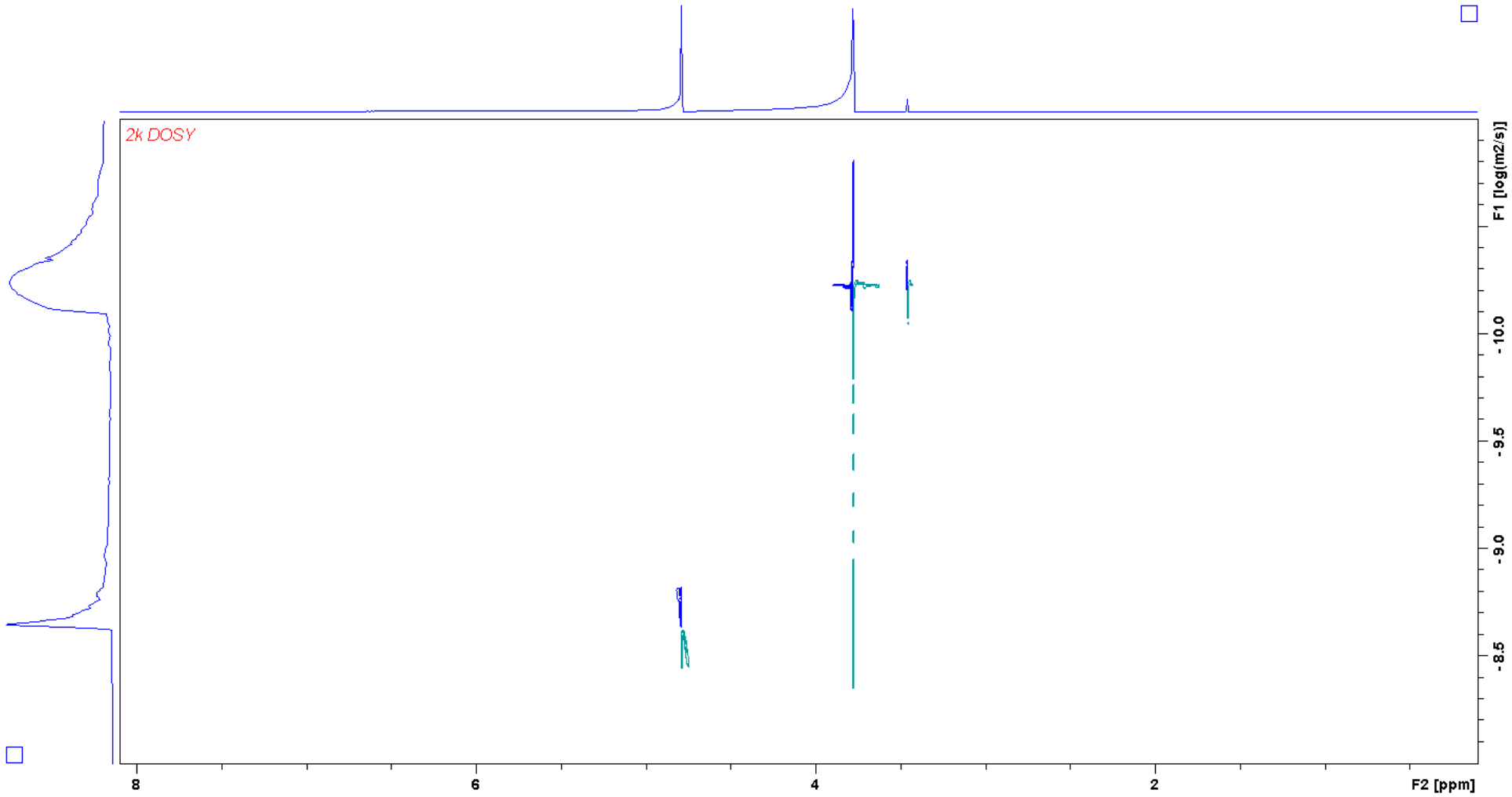
2D DOSY ^{1}H NMR

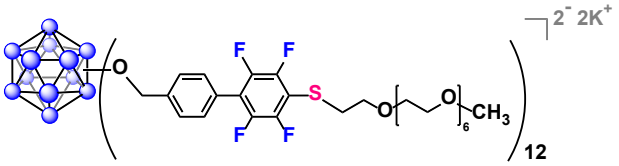
BRUKER



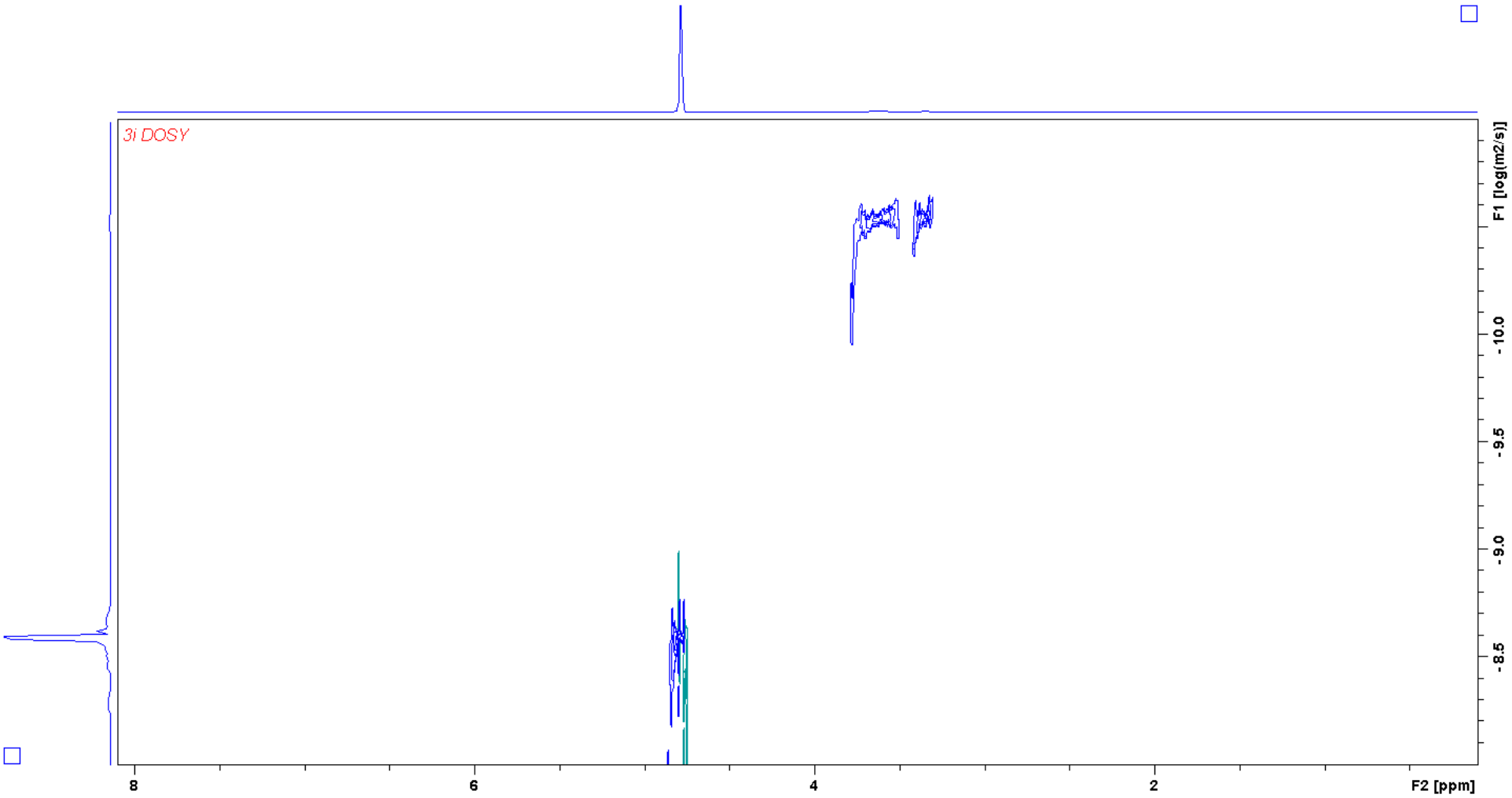


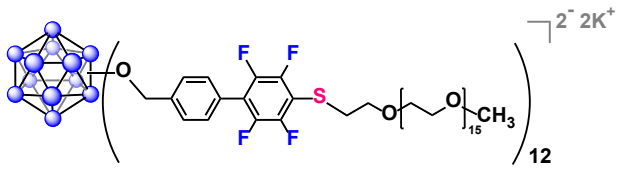
2D DOSY ^{1}H NMR



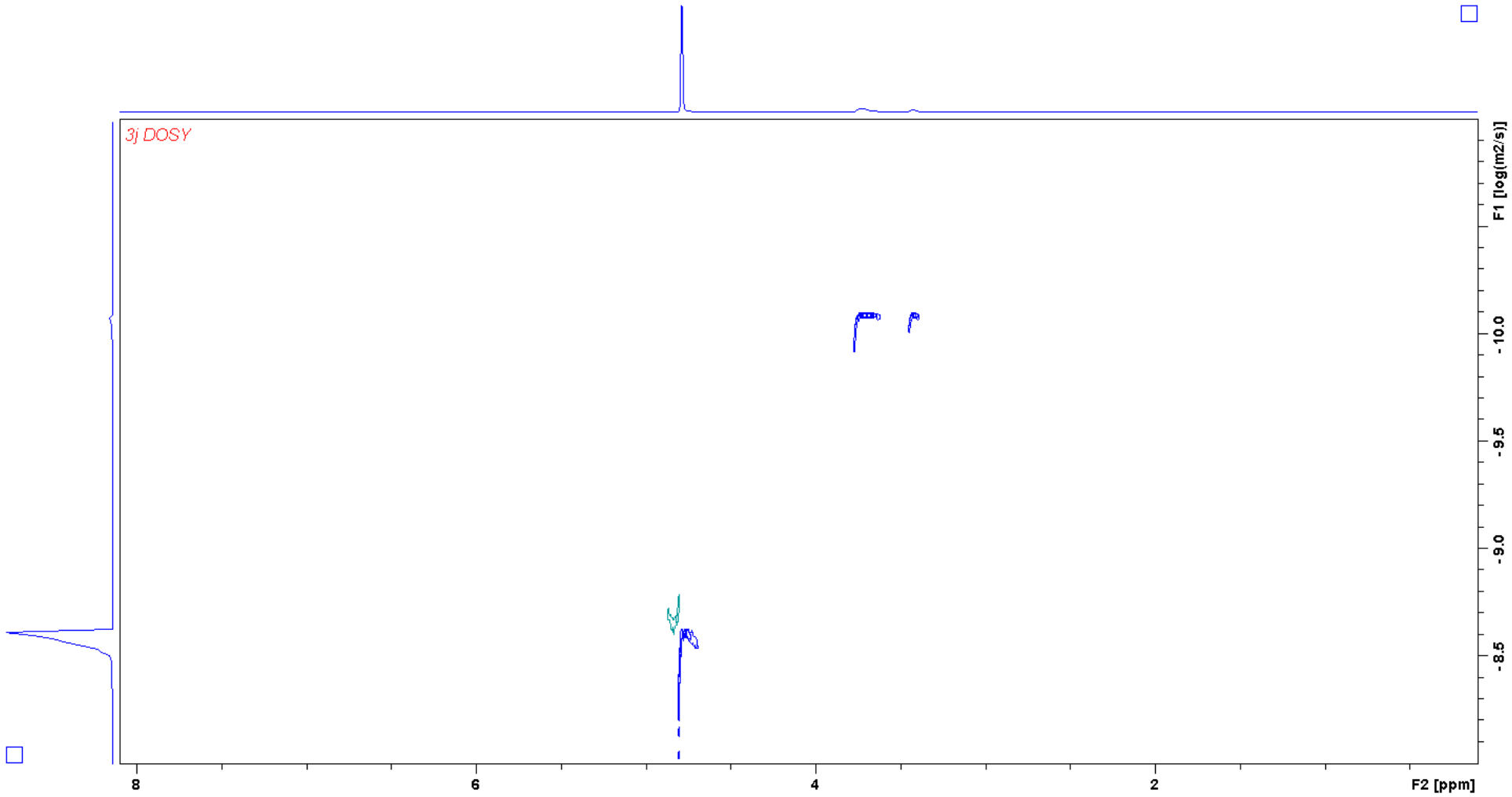


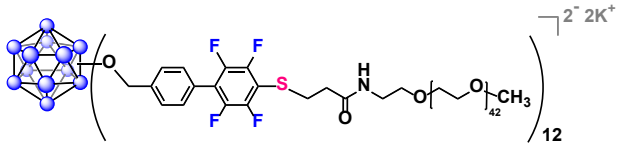
2D DOSY ^{1}H NMR



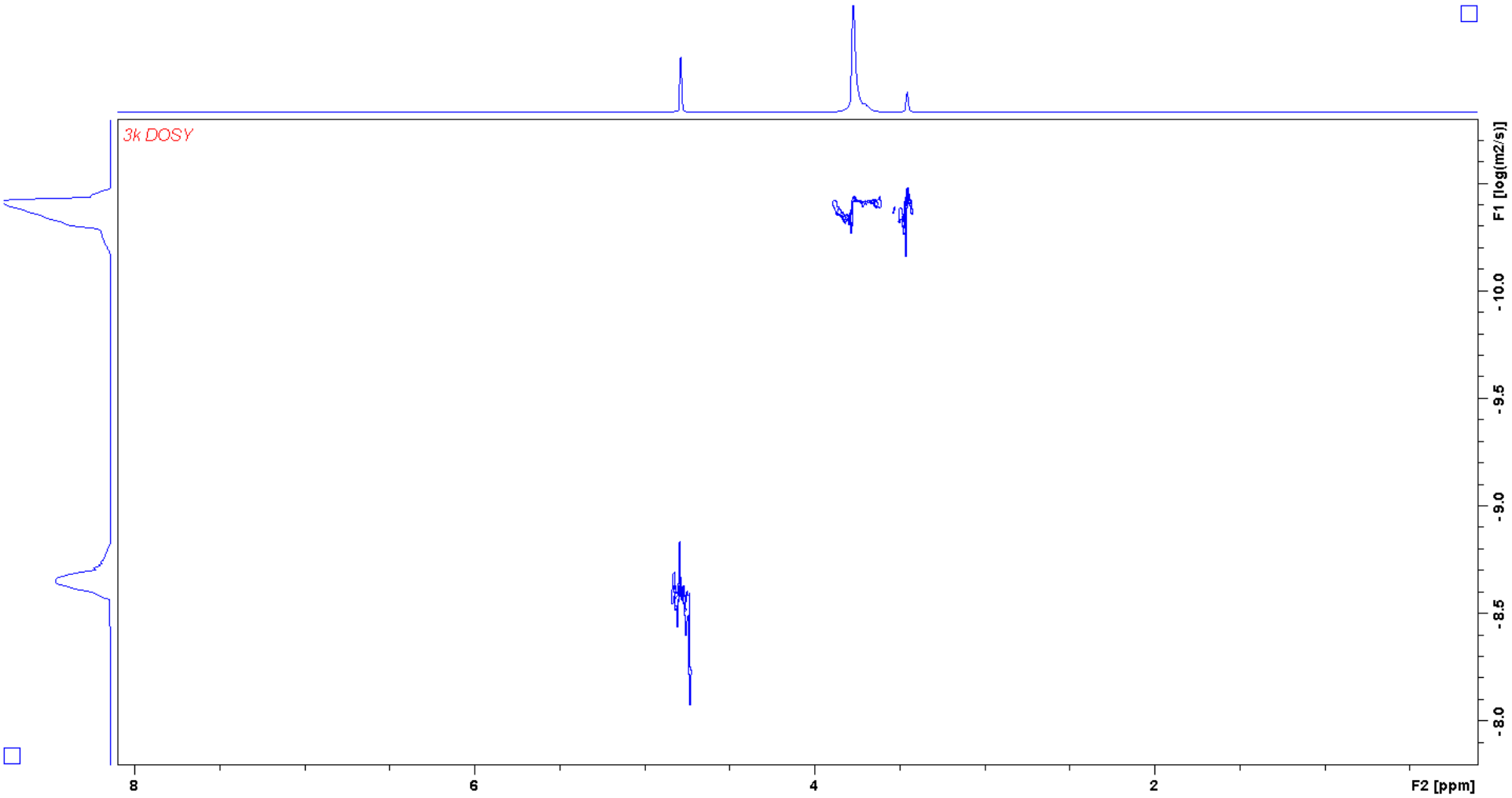


2D DOSY ^{1}H NMR





2D DOSY ^{1}H NMR



Stability studies of 2i under biologically relevant conditions

Cell culture media/fetal bovine serum: 14.8 mg of **2i** was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of serum media (440 μL cell culture media and 60 μL fetal bovine serum). This mixture was vortexed and then transferred to an NMR tube and monitored over 5 days at room temperature by ^{11}B and ^{19}F NMR spectroscopy. This sample was then incubated at 37 °C for an additional 5 days and subjected to analysis *via* ^{11}B and ^{19}F NMR spectroscopy. No significant change was observed by NMR spectroscopy.

pH 5: 14.8 mg of **2i** was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of a 0.1 M citric acid/sodium citrate buffer at pH 5.0. This mixture was vortexed and then transferred to an NMR tube and monitored over 5 days at room temperature by ^{11}B and ^{19}F NMR spectroscopy. NMR spectroscopy suggests that the structural integrity is maintained. We note that we observed small impurities corresponding to boric acid and borates by ^{11}B NMR spectroscopy as well as some peak broadening in ^{11}B and ^{19}F NMR spectra due to the oxidation of **2i** from the 2- to the 1- oxidation state over time.

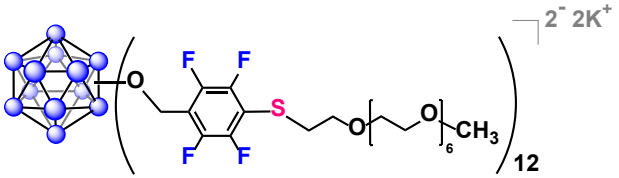
pH 7: 14.8 mg of **2i** was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of a 0.1 M Tris/HCl buffer at pH 7.0. This mixture was vortexed and then transferred to an NMR tube and monitored over 5 days at room temperature by ^{11}B and ^{19}F NMR spectroscopy. NMR spectroscopy suggests that the structural integrity is maintained. We note that we observed small impurities corresponding to boric acid and borates by ^{11}B NMR spectroscopy as well as some peak broadening in ^{11}B and ^{19}F NMR spectra due to the oxidation of **2i** from the 2- to the 1- oxidation state over time.

pH 9: 14.8 mg of **2i** was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of a 0.1 M Tris/HCl buffer at pH 9.0. This mixture was vortexed and then transferred to

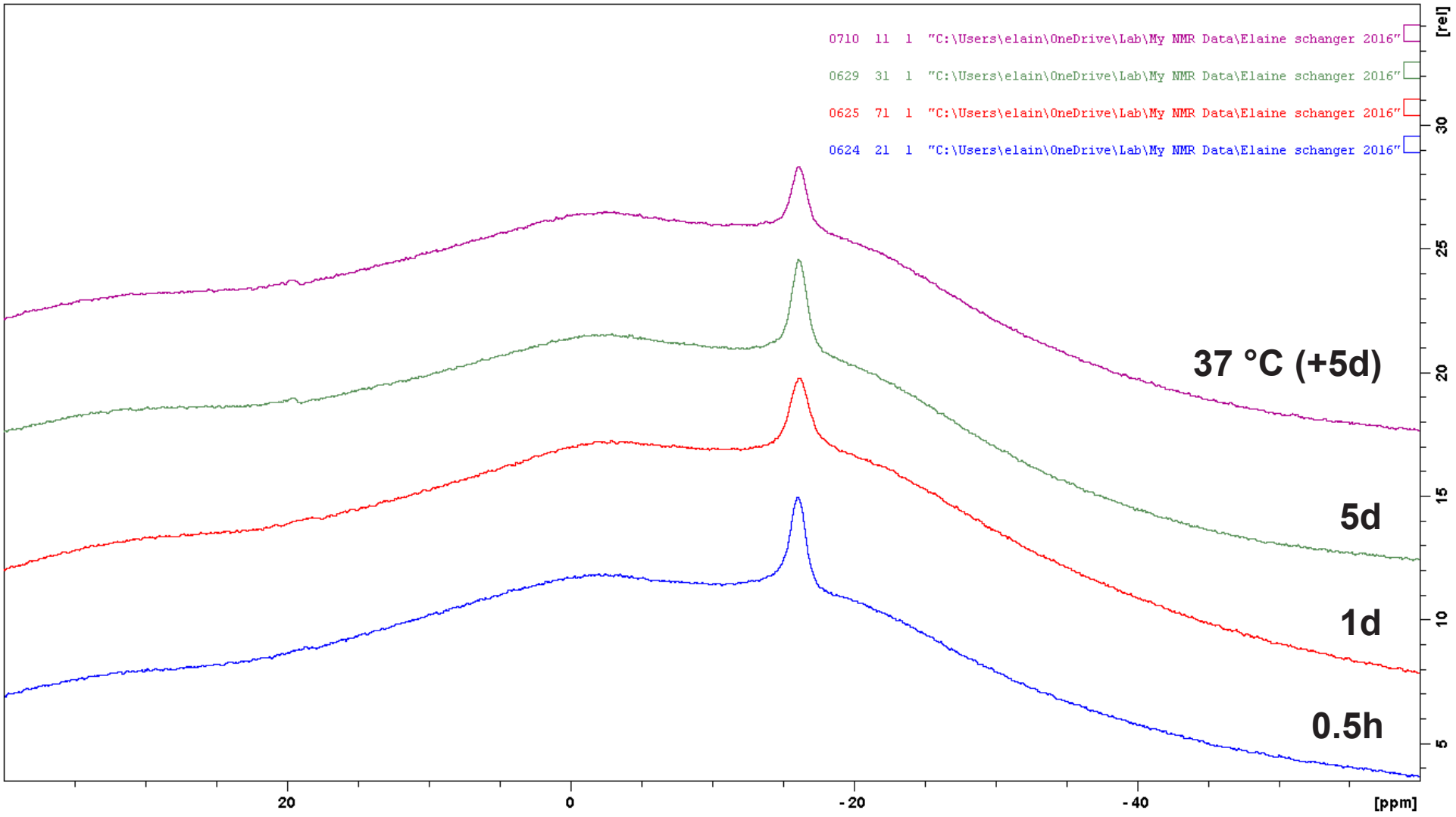
an NMR tube and monitored over 5 days at room temperature by ^{11}B and ^{19}F NMR spectroscopy. NMR spectroscopy suggests that the structural integrity is maintained. We note that we observed small impurities corresponding to borates by ^{11}B NMR spectroscopy as well as some peak broadening in ^{11}B and ^{19}F NMR spectra due to the oxidation of **2i** from the 2- to the 1- oxidation state over time.

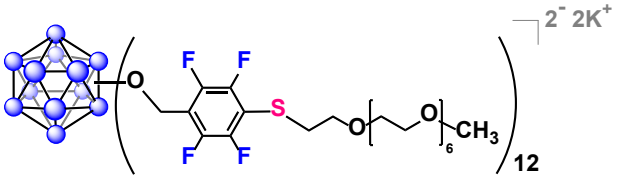
2-Mercaptoethanol: 16.9 mg of **2i** was dissolve in 2.82 mL of D_2O. 500 μL of this solution was added to 100 μL of a 120 mM 2-mercaptoethanol D_2O solution. This mixture was vortexed and then transferred to an NMR tube and monitored over 11 days at room temperature by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy. After 11 days, this sample was subjected to mass spectrometry analysis. Both NMR spectroscopy and mass spectrometry suggest that the structural integrity is maintained. We note that we observed a small boric acid impurity by ^{11}B NMR spectroscopy.

Glutathione: 16.9 mg of **2i** was dissolve in 2.82 mL of D_2O. 500 μL of this solution was added to 100 μL of a 12 mM glutathione D_2O solution. This mixture was vortexed and then transferred to an NMR tube and monitored over 11 days at room temperature by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy. After 11 days, this sample was subjected to mass spectrometry analysis. Both NMR spectroscopy and mass spectrometry suggest that the structural integrity is maintained. We note that we observed a small boric acid impurity by ^{11}B NMR spectroscopy as well as some peak broadening in ^{11}B and ^{19}F NMR spectra due to the oxidation of **2i** from the 2- to the 1- oxidation state over time.

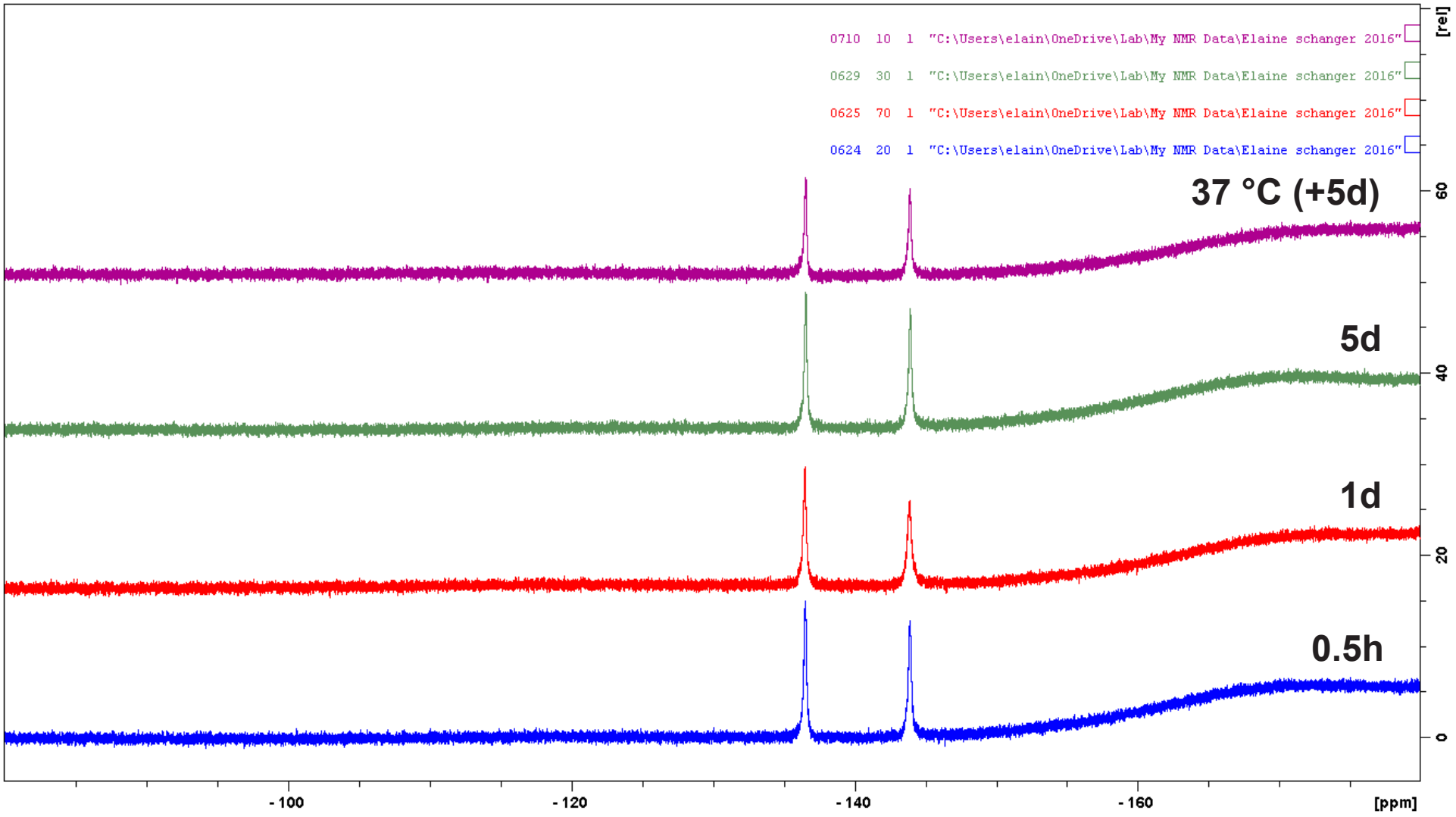


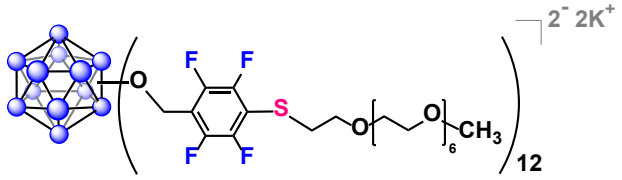
Stability of 2i in Serum
^{11}B NMR



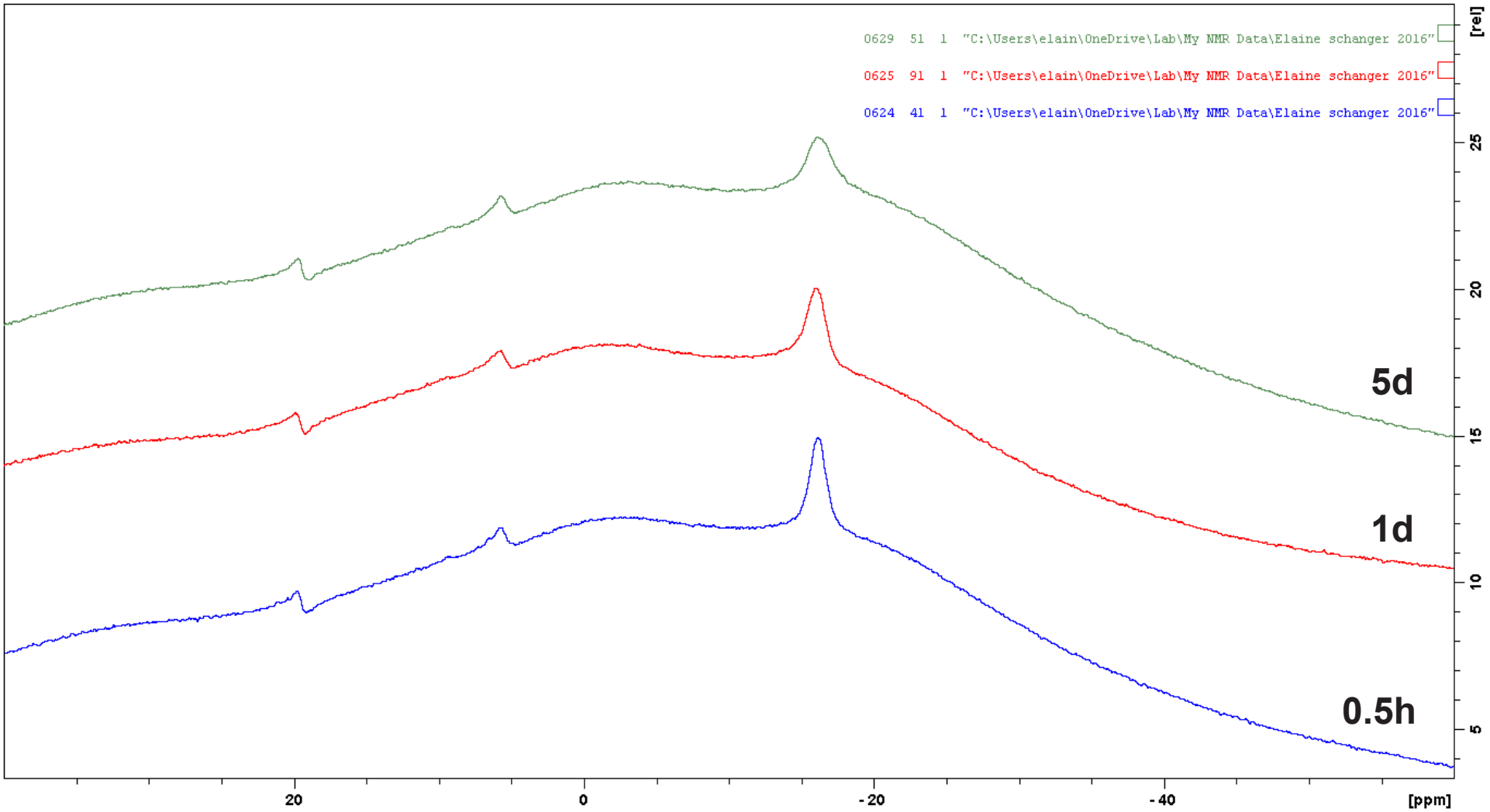


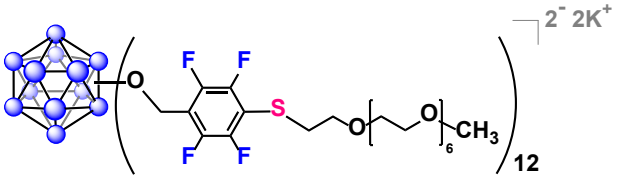
Stability of 2i in Serum
^{19}F NMR



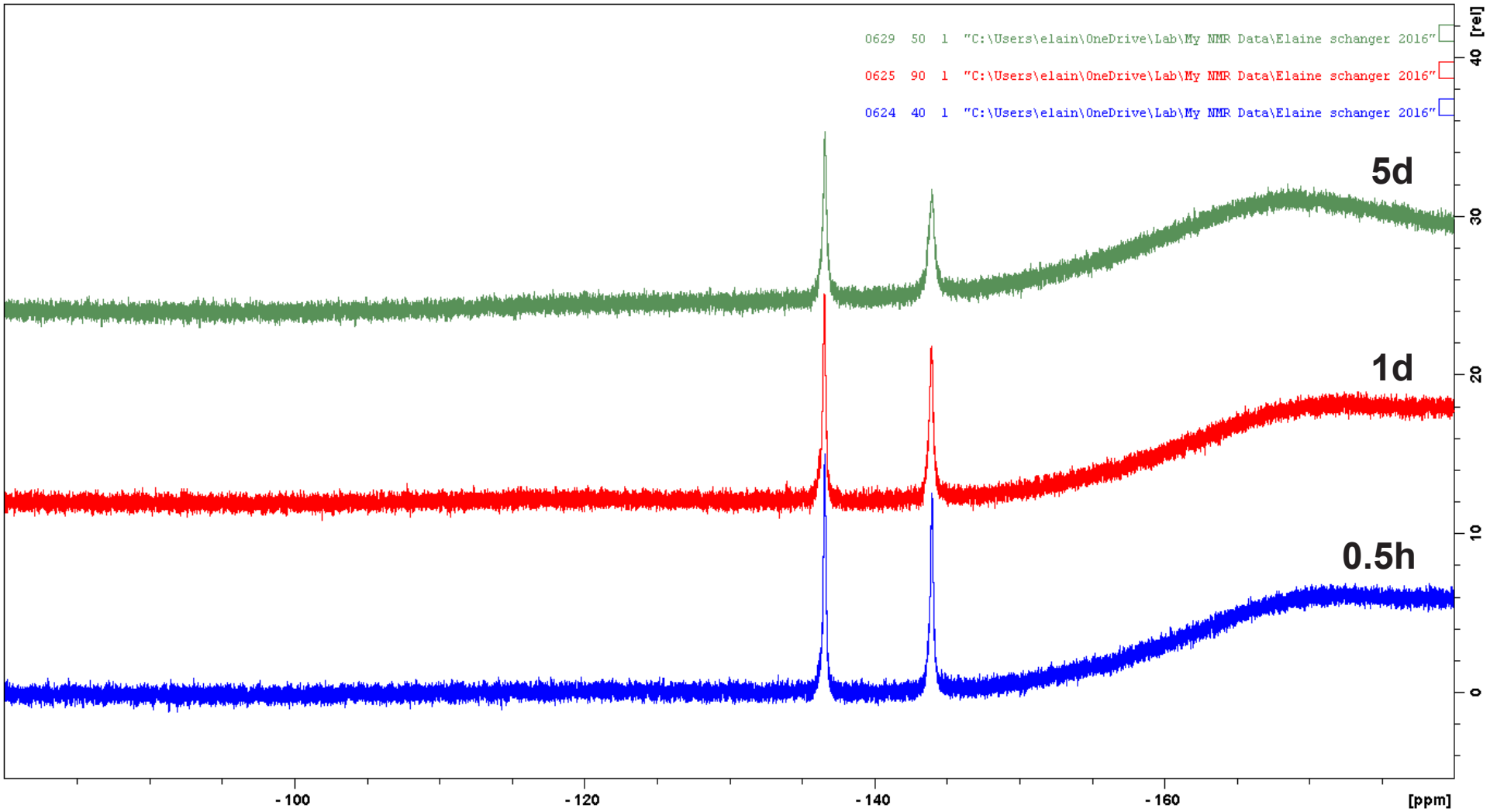


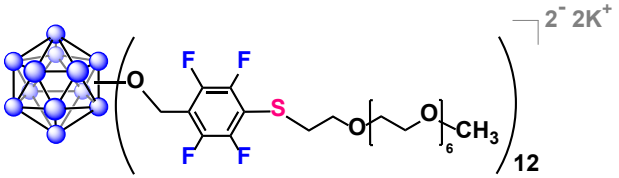
Stability of 2i at pH 5
^{11}B NMR



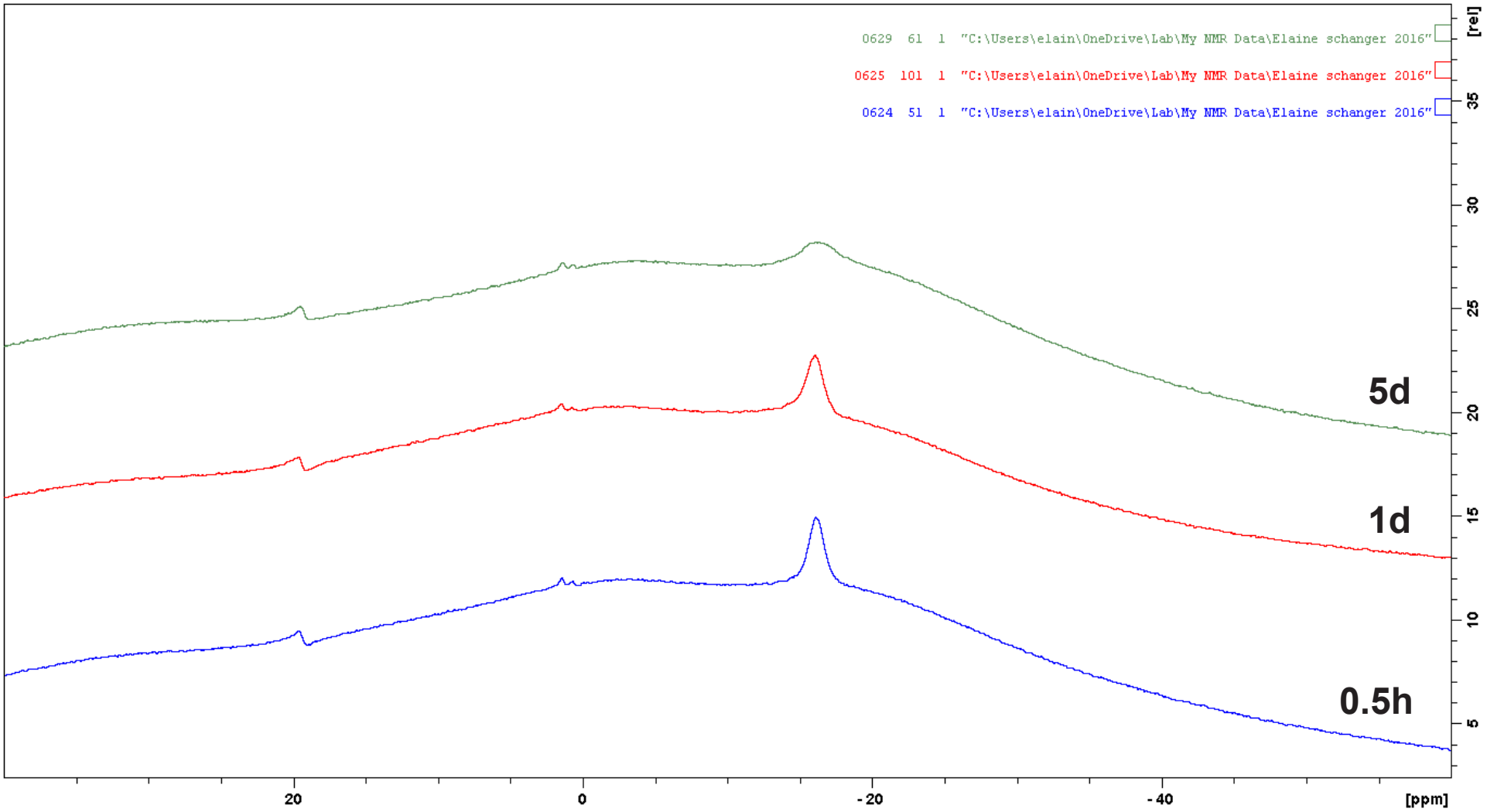


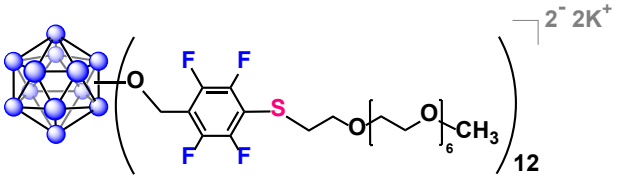
Stability of 2i at pH 5
^{19}F NMR



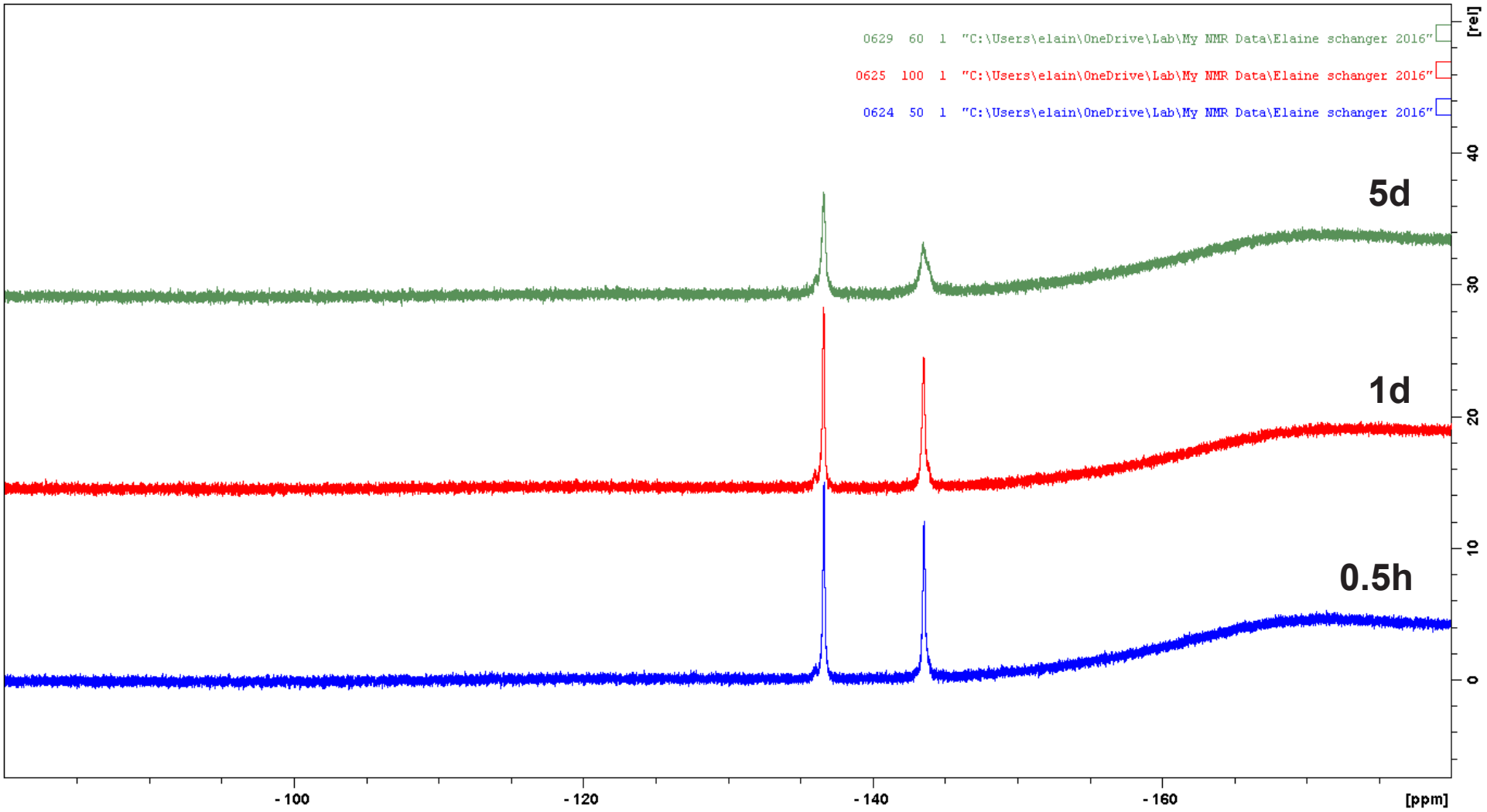


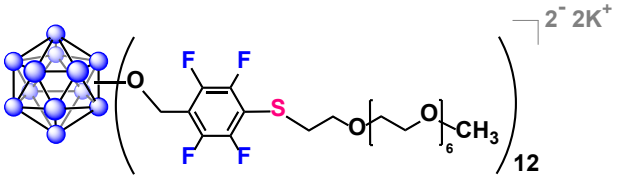
Stability of 2i at pH 7
^{11}B NMR



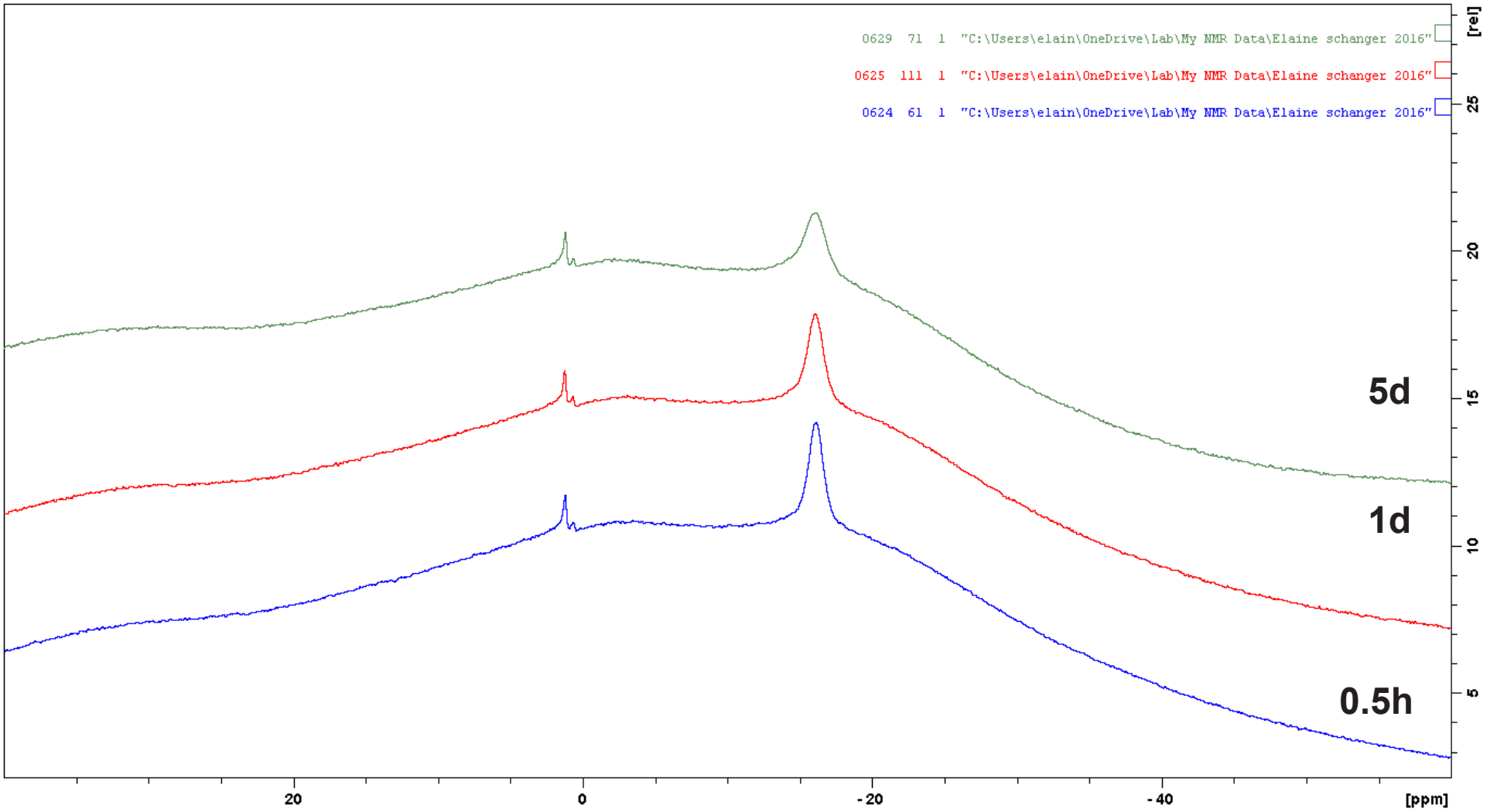


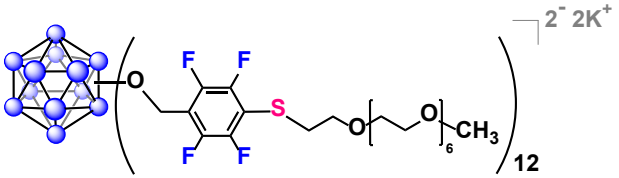
Stability of 2i at pH 7
^{19}F NMR



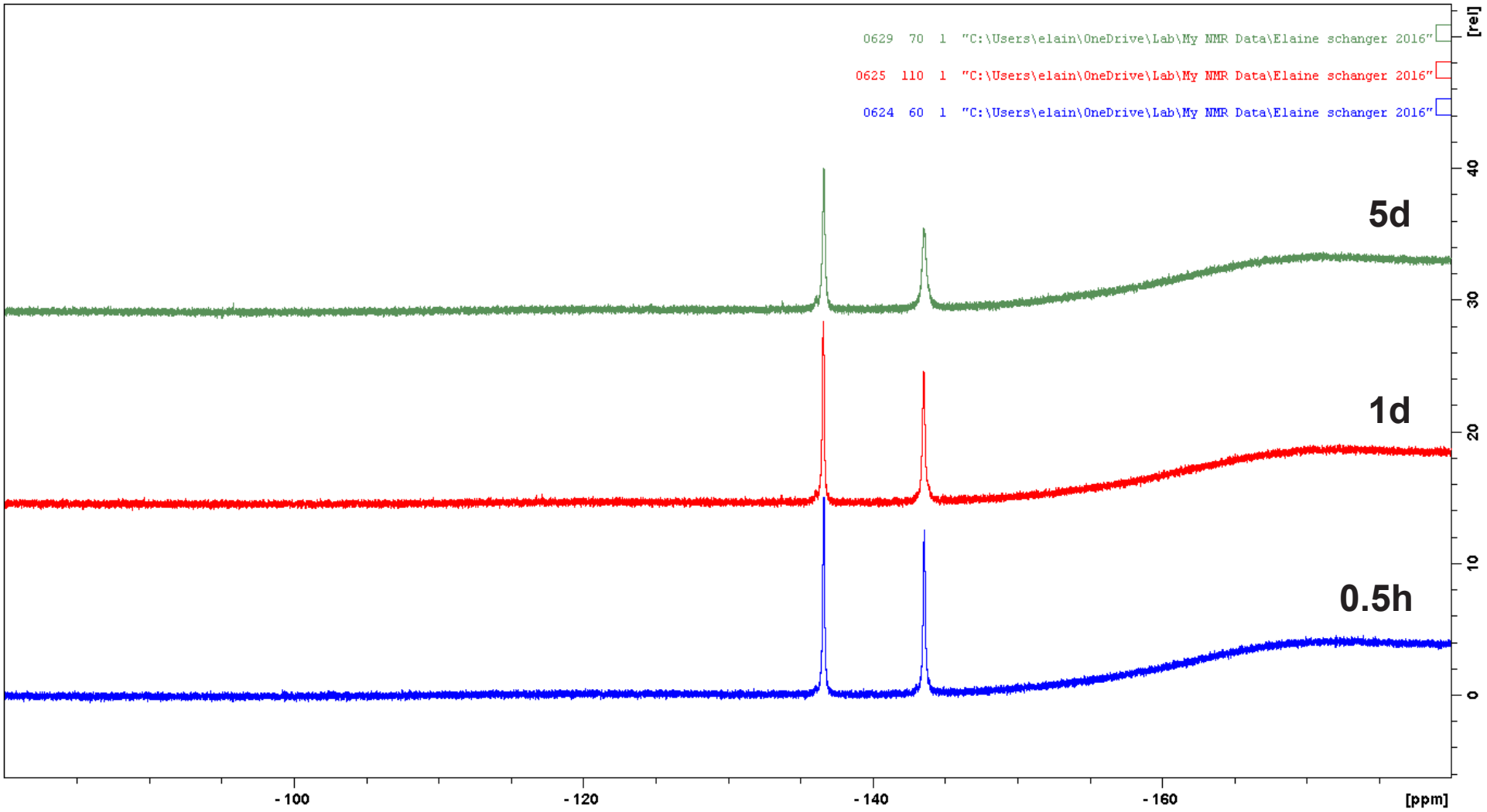


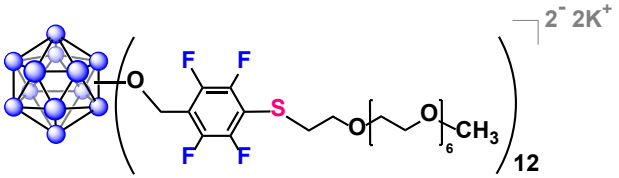
Stability of 2i at pH 9
^{11}B NMR



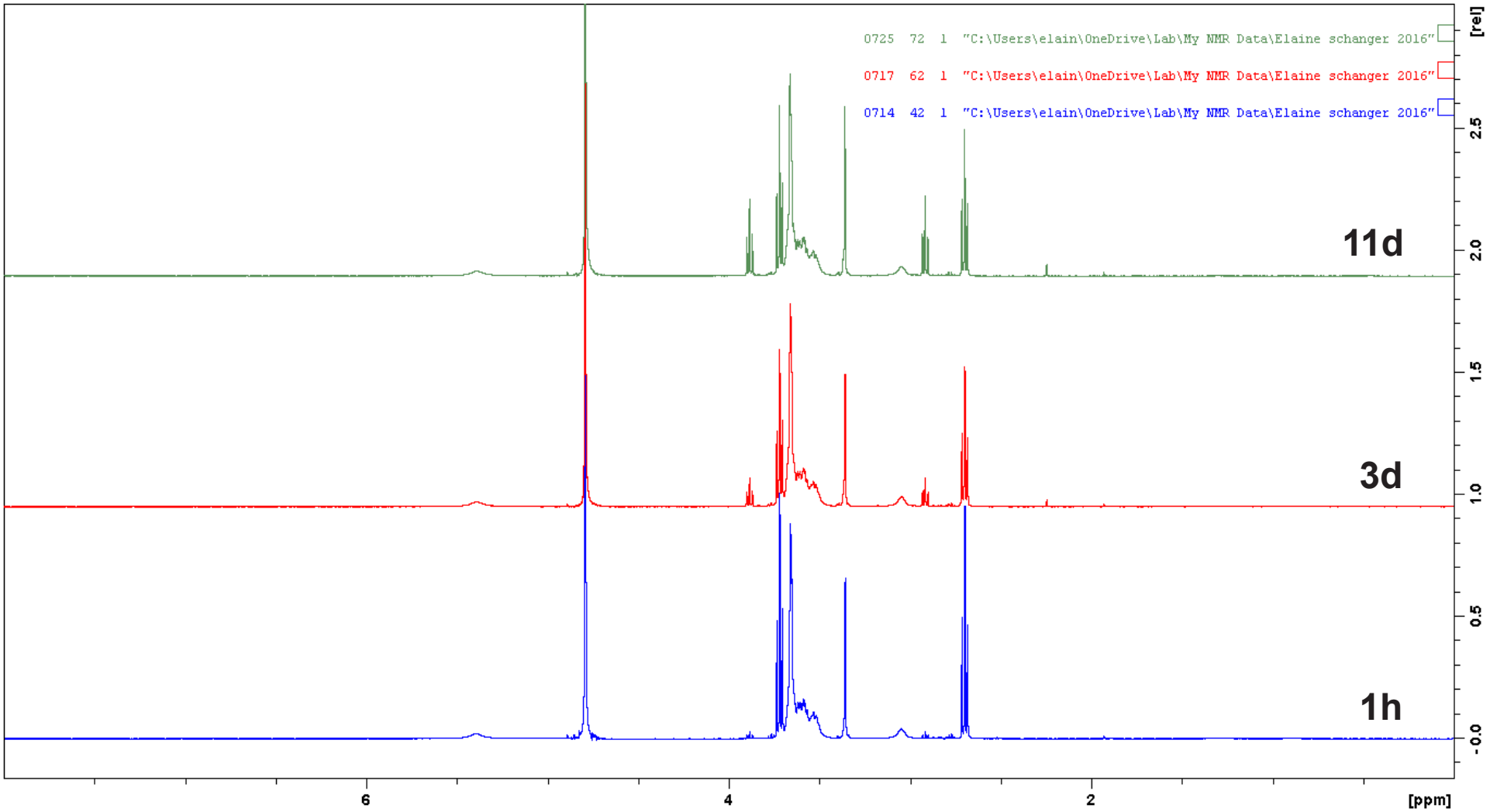


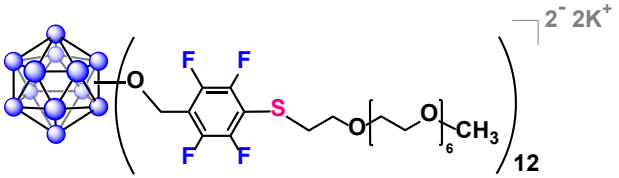
Stability of 2i at pH 9
^{19}F NMR



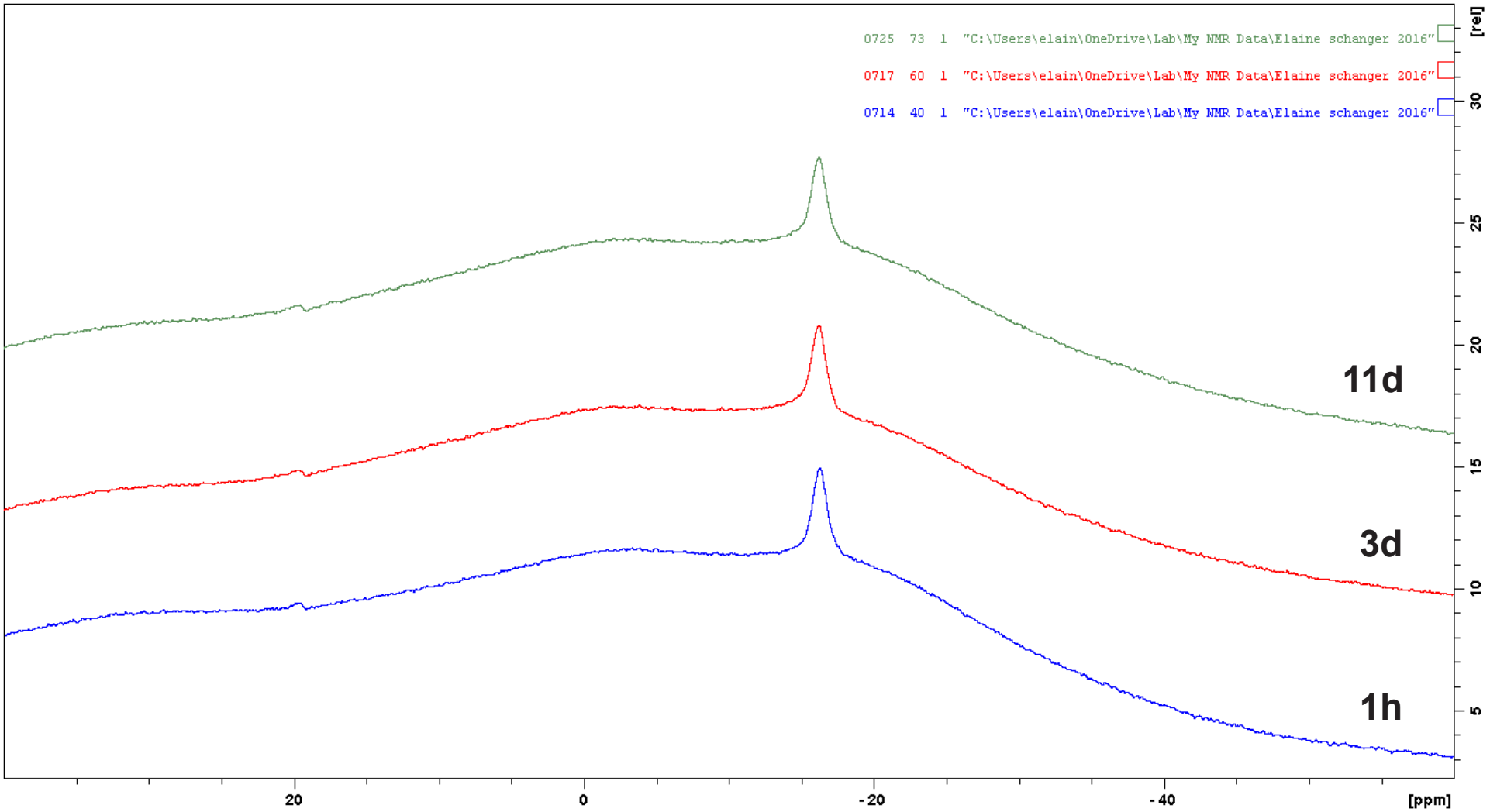


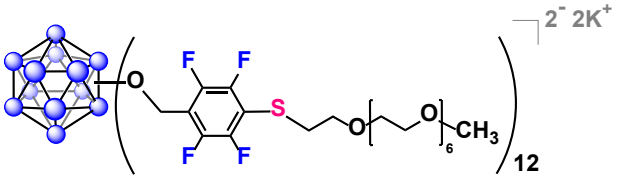
Stability of 2i in 2-Mercaptoethanol
^{1}H NMR



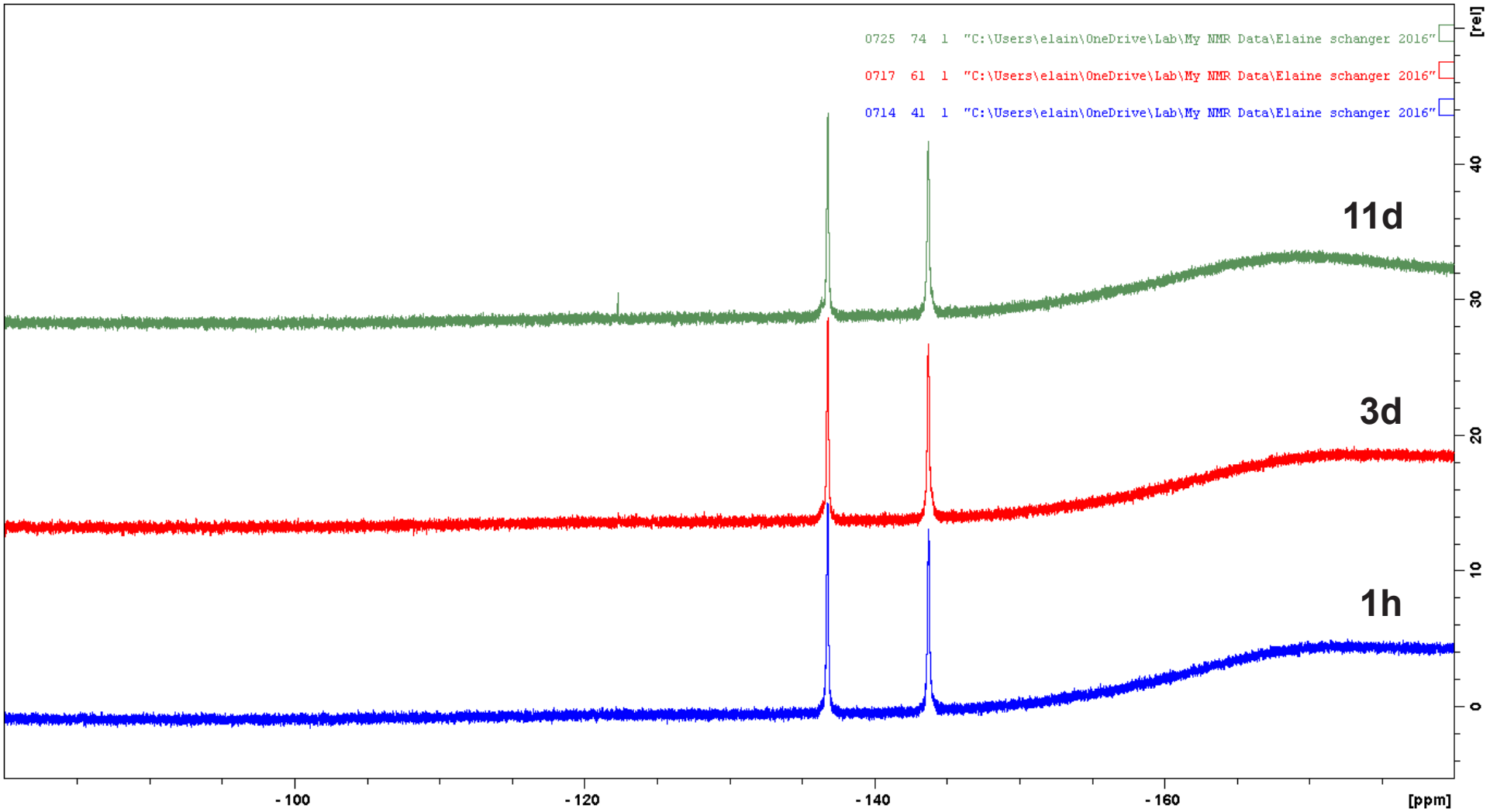


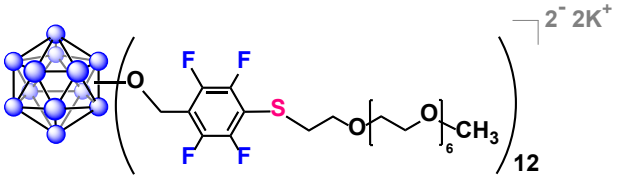
Stability of 2i in 2-Mercaptoethanol
^{11}B NMR



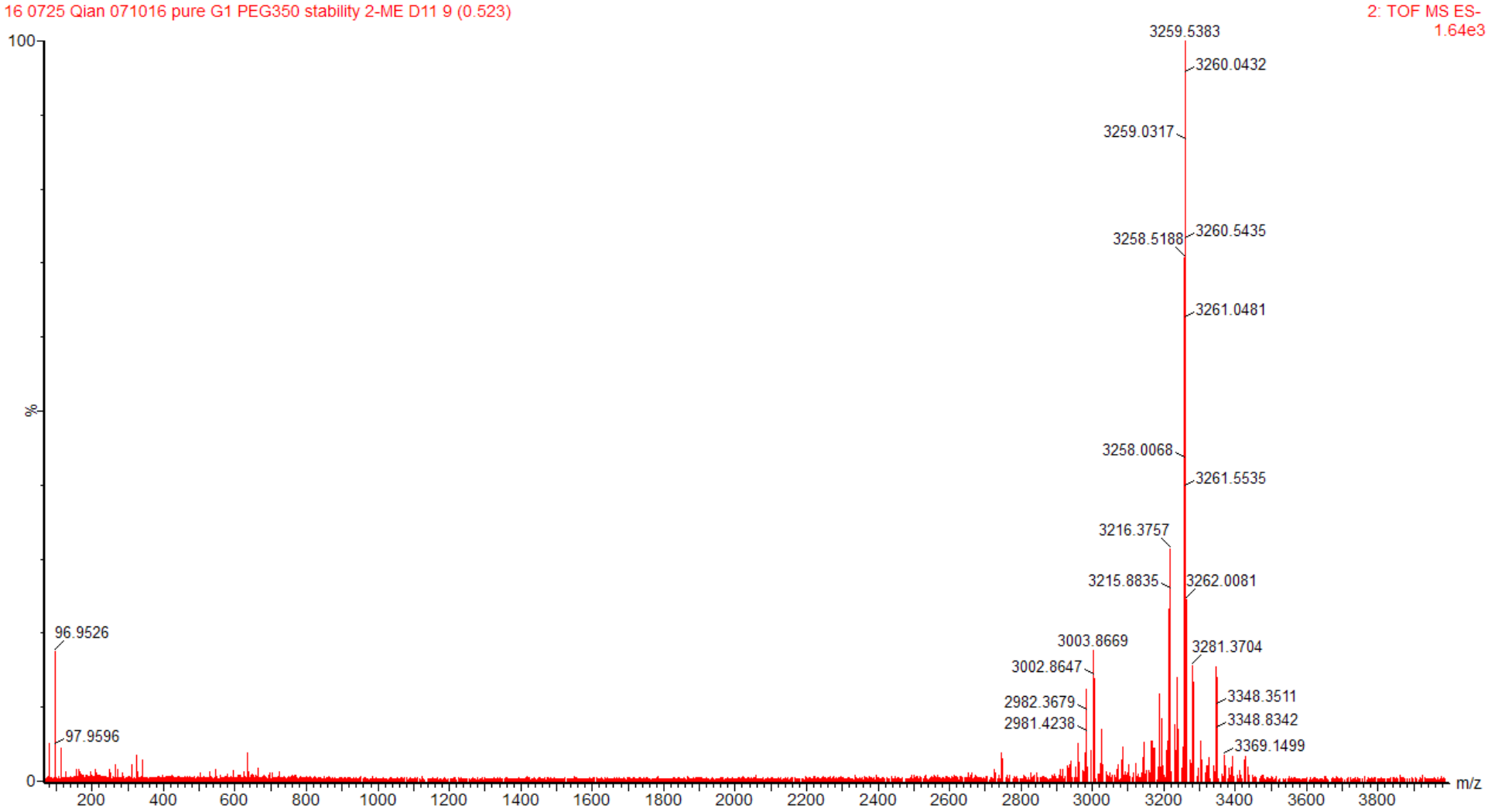


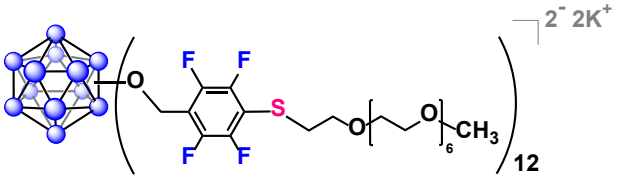
Stability of 2i in 2-Mercaptoethanol
^{19}F NMR



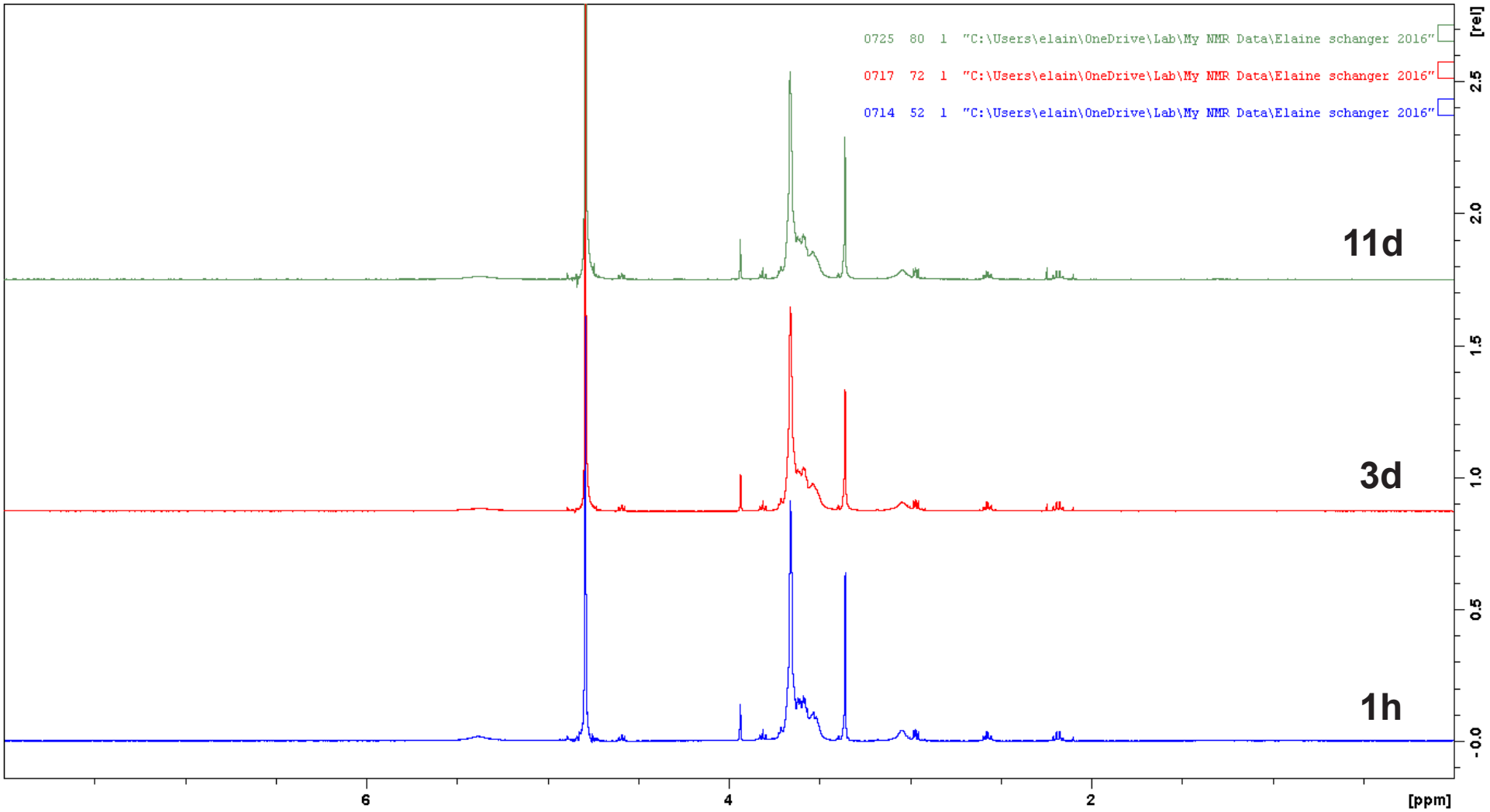


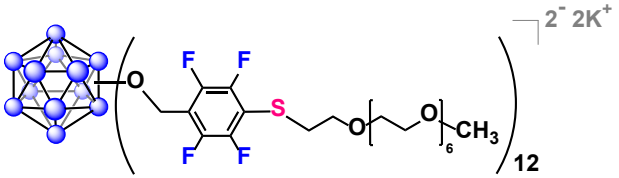
Stability of 2i in 2-Mercaptoethanol - Day 11
Waters Mass Spec



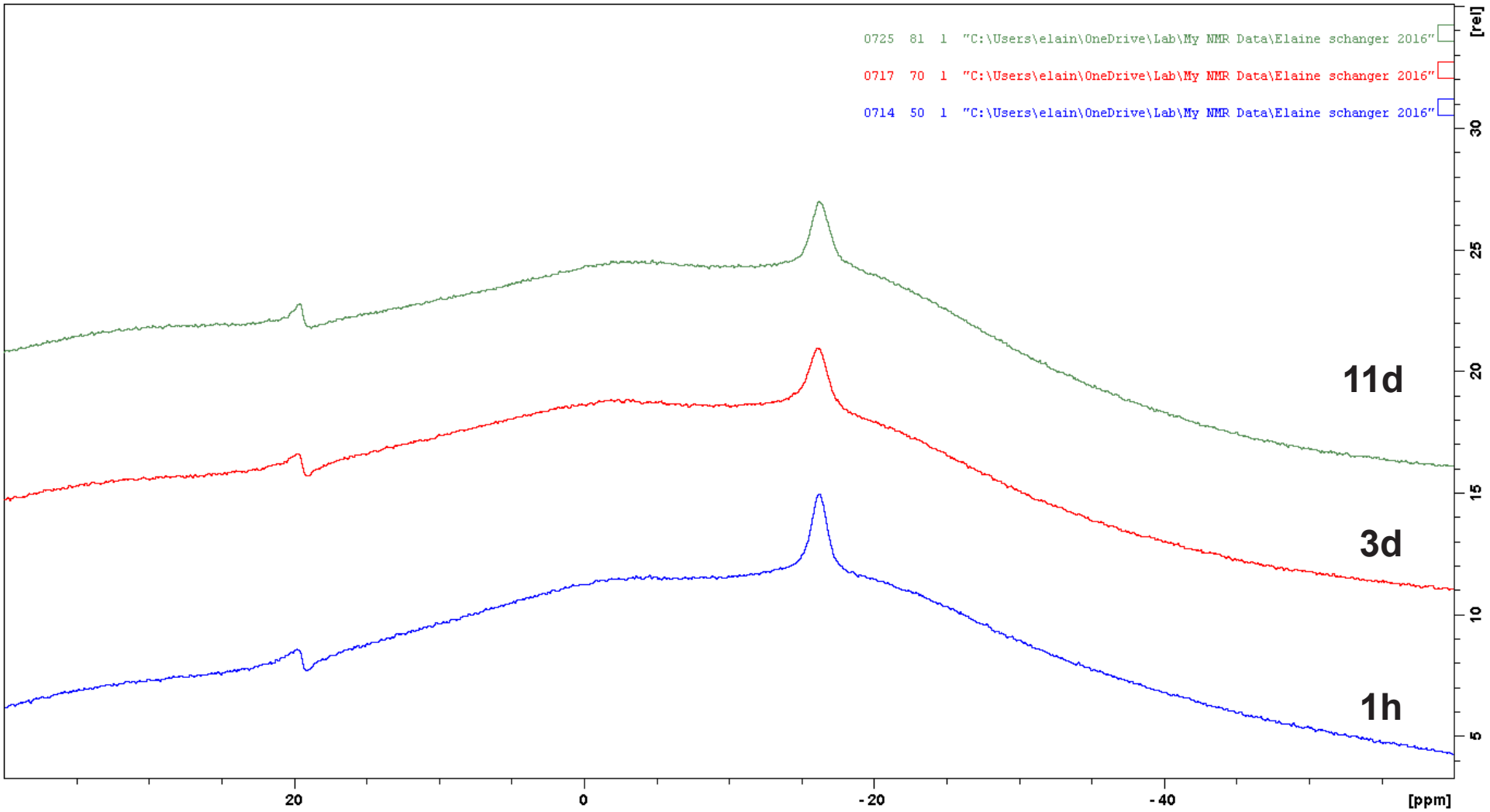


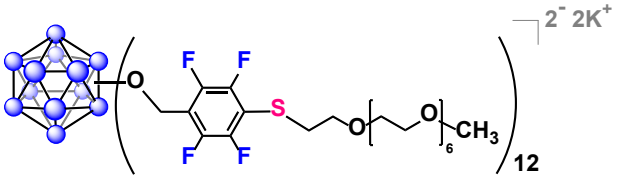
Stability of 2i in Glutathione
^{1}H NMR



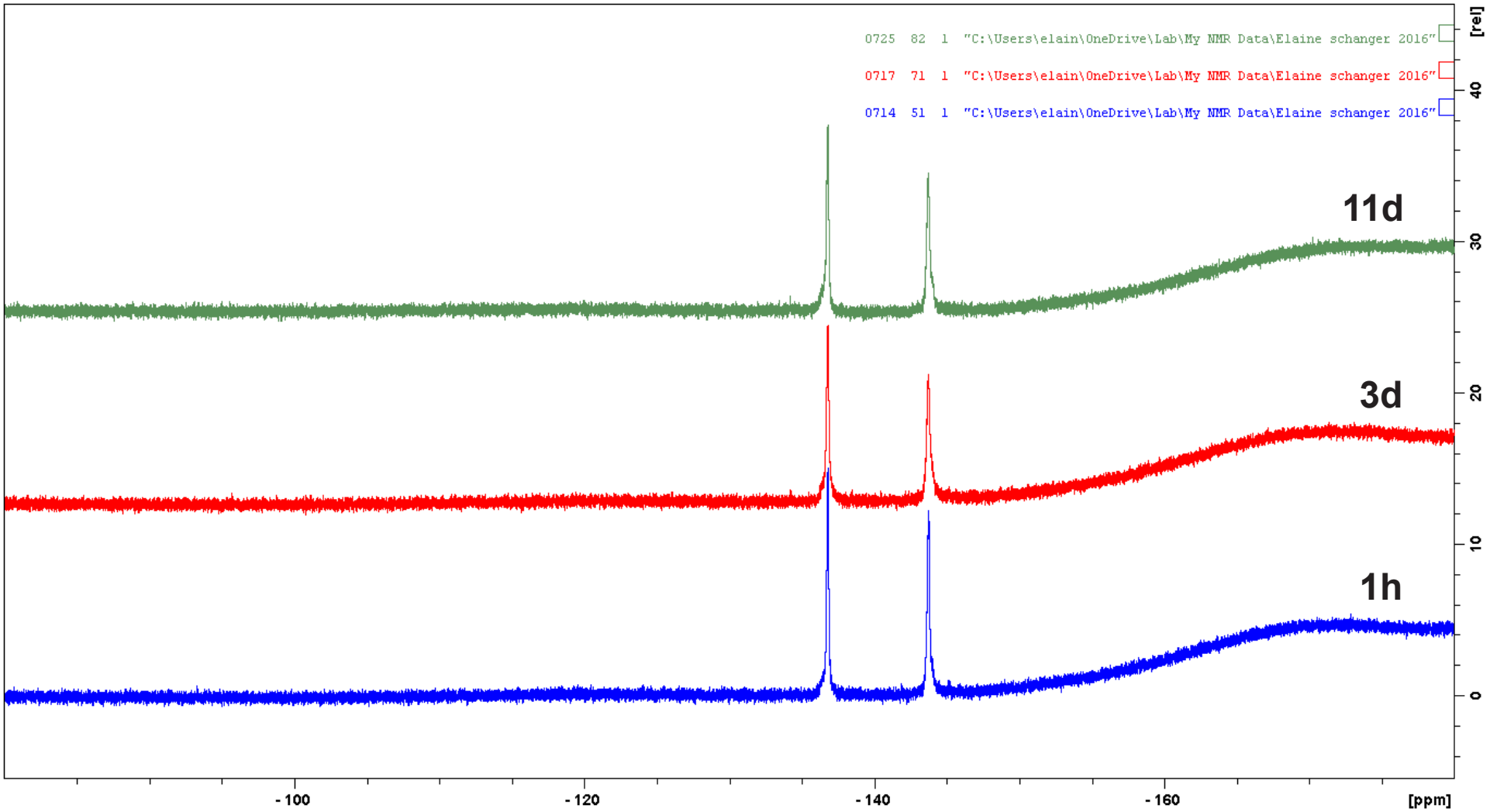


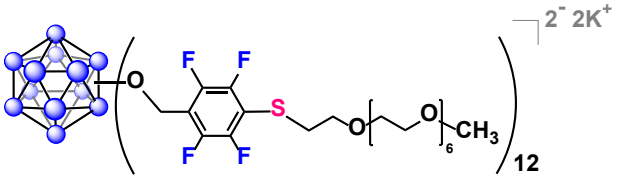
Stability of 2i in Glutathione
^{11}B NMR





Stability of 2i in Glutathione
^{19}F NMR

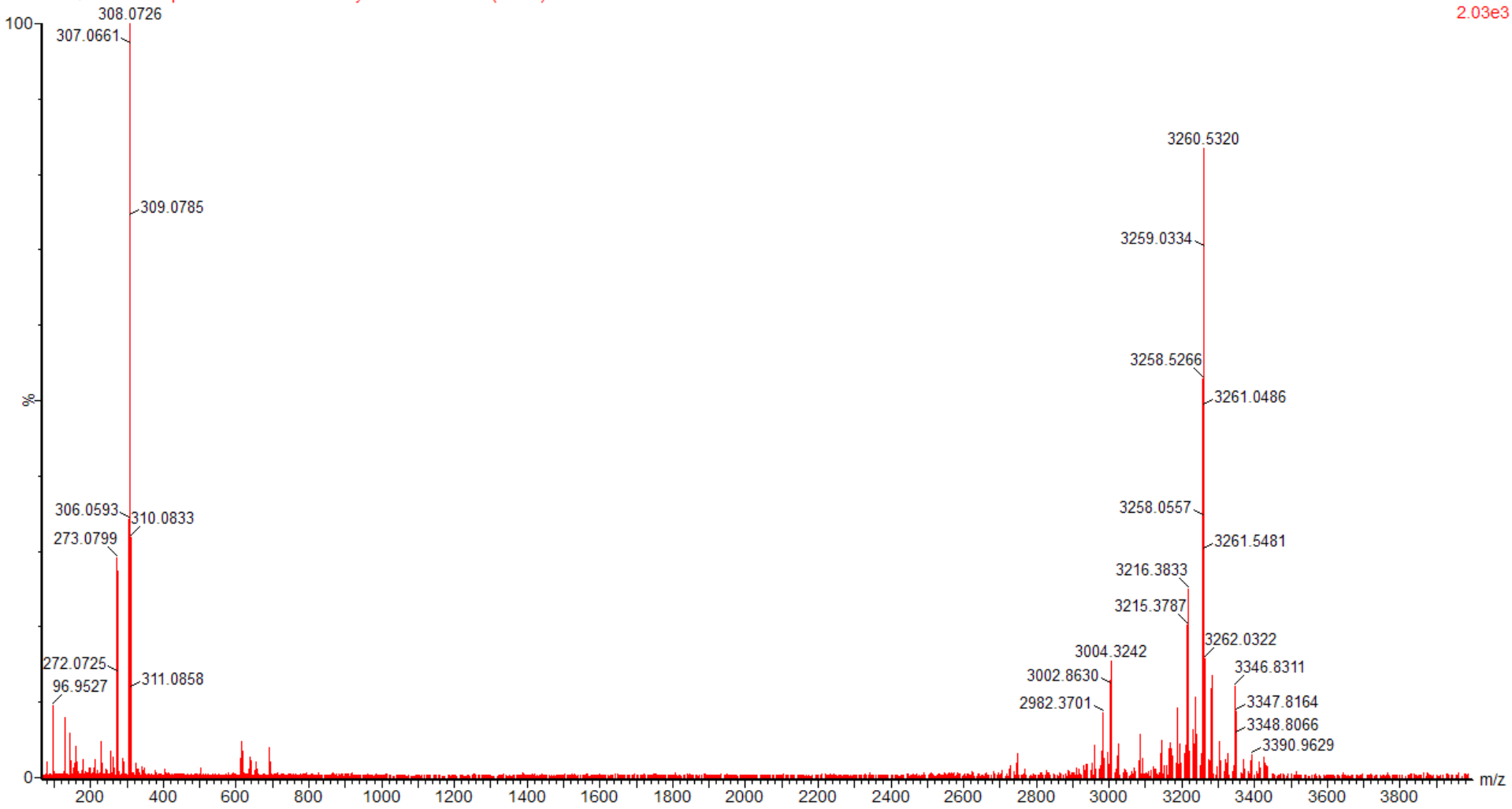




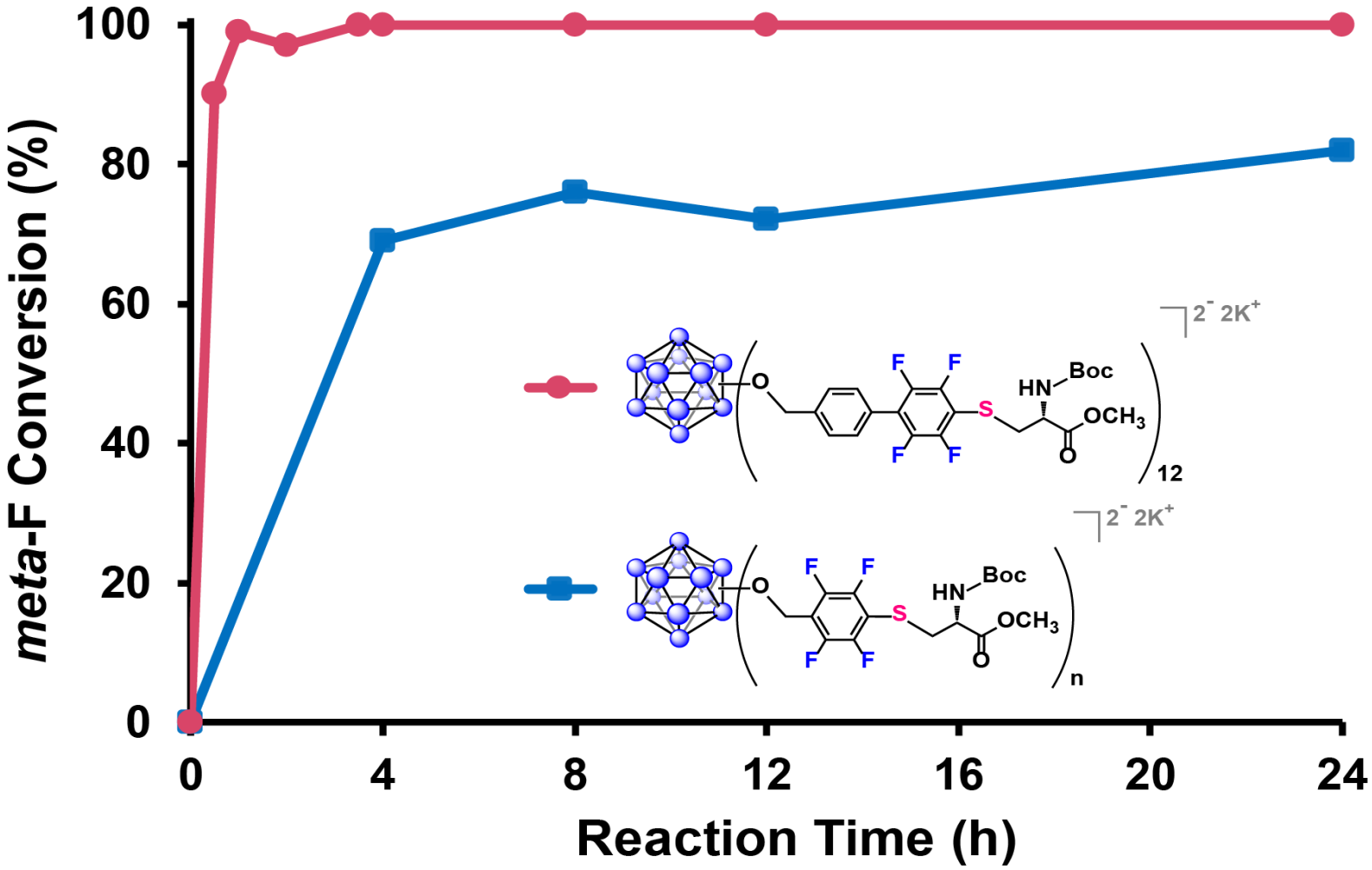
Stability of 2i in Glutathione - Day 11
Waters Mass Spec

16 0725 Qian 071016 pure G1 PEG350 stability GSH D11 121 9 (0.523)

2: TOF MS ES-
2.03e3



Plot of Conjugation Progress of Boc-cysteine (g) onto Clusters 2/3



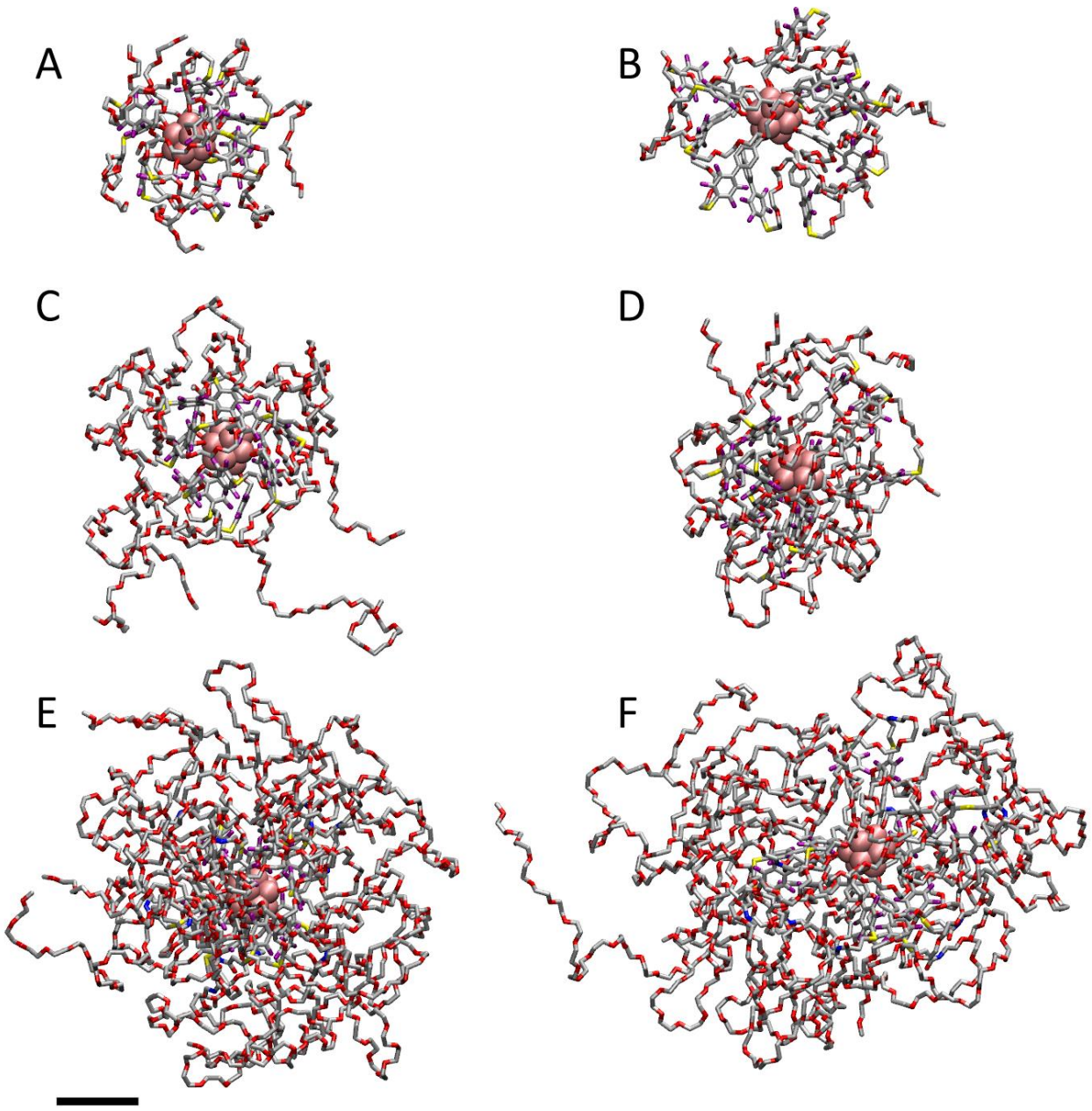
Computational work

A. PEGylated OCNs

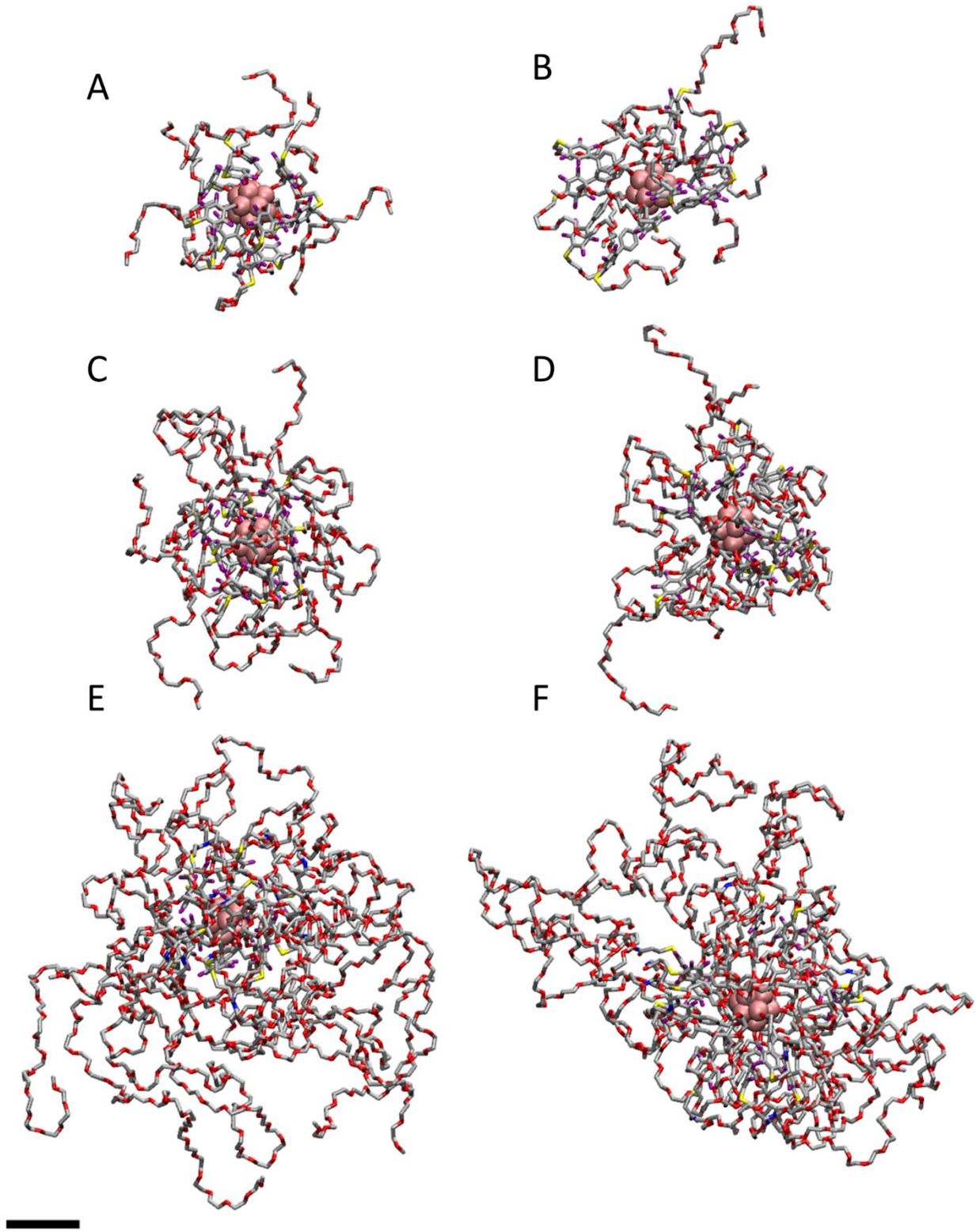
PEGylated nanoparticles (NPs) **2i–k** and **3i–k** (see Table 2) were modeled using molecular dynamics (MD) simulations in: *i)* water with counter ions and *ii)* a buffer solution of HPO_4^{2-} and $H_2PO_4^-$ at a total 0.08 M concentration, where the ratio of the two ions was used matched pH 7.4. The MD simulations were performed with NAMD[10], using the CHARMM force field[11–16]. *Ab initio* calculations were done with Gaussian09[17] to determine unknown parameters for the dodecaborate cluster center and the non-PEGylated (**2** or **3** type ligand) section of the ligand. The boron center was optimized using a HF/6-31g level of theory, with partial charges derived with a ChelpG algorithm[18]. Bonds, angles, and dihedrals force constants containing boron atoms were chosen to have relatively large values, approximately equal to those of double bonded or aromatic carbons, so that the boron center would be rigid. The type **2** and **3** ligands had their bond and angle parameters determined at the MP2/6-31g(d)//HF/6-31g level of theory with VMD Force Field Toolkit plugin[19]. Unknown dihedral parameters were chosen based on similar atom types in the CHARMM force field[11–16]. Partial charges were determined through the ChelpG aglorithm[18]. Amide and PEGylated geometries, parameters, and charges were taken from the CHARMM force field[11–16].

Each of the 6 NPs was separately simulated in water and ionic solutions. Each system is first minimized for 10,000 steps. Afterwards it is heated to 310 K, with 1 K increments per 20 steps until the system reaches a temperature of 310 K, when a pre-equilibration is done. Simulations are performed in an NPT ensemble, at 310 K and a pressure of 1 atm, with Langevin dynamics and a damping constant of 0.01 ps^{-1}. Langevin piston is used with a period of 200 fs and decay of 100 fs. Particle Mesh Ewald[20] is used for long range electrostatic interactions with a grid

spacing of 1.0. Short range interactions are performed with the 12-6 Lennard-Jones potential, using a switching function. Velocity Verlet integration is used with the SHAKE algorithm and a time step of 2 fs. Data and snapshots are recorded every 10 ps or 5,000 steps. Simulation times of 25 ns for the water solution and 30 ns for the salt system were used, respectively. Supplementary Figures 1 and 2 show snapshots of PEGylated NPs in water (21 ns) and in the ionic solution (31 ns), respectively. Notice that as the chain length increases, the chains are fluctuating significantly to the extent that the chain distributions become asymmetric. In the following, we describe some characteristics of these systems.



Supplementary Figure 1. Nanoparticles snapshots in water after 21 ns of simulations. Scale bar is 1 nm. A) **2i** B) **3i** C) **2j** D) **3j** E) **2k** F) **3k**.

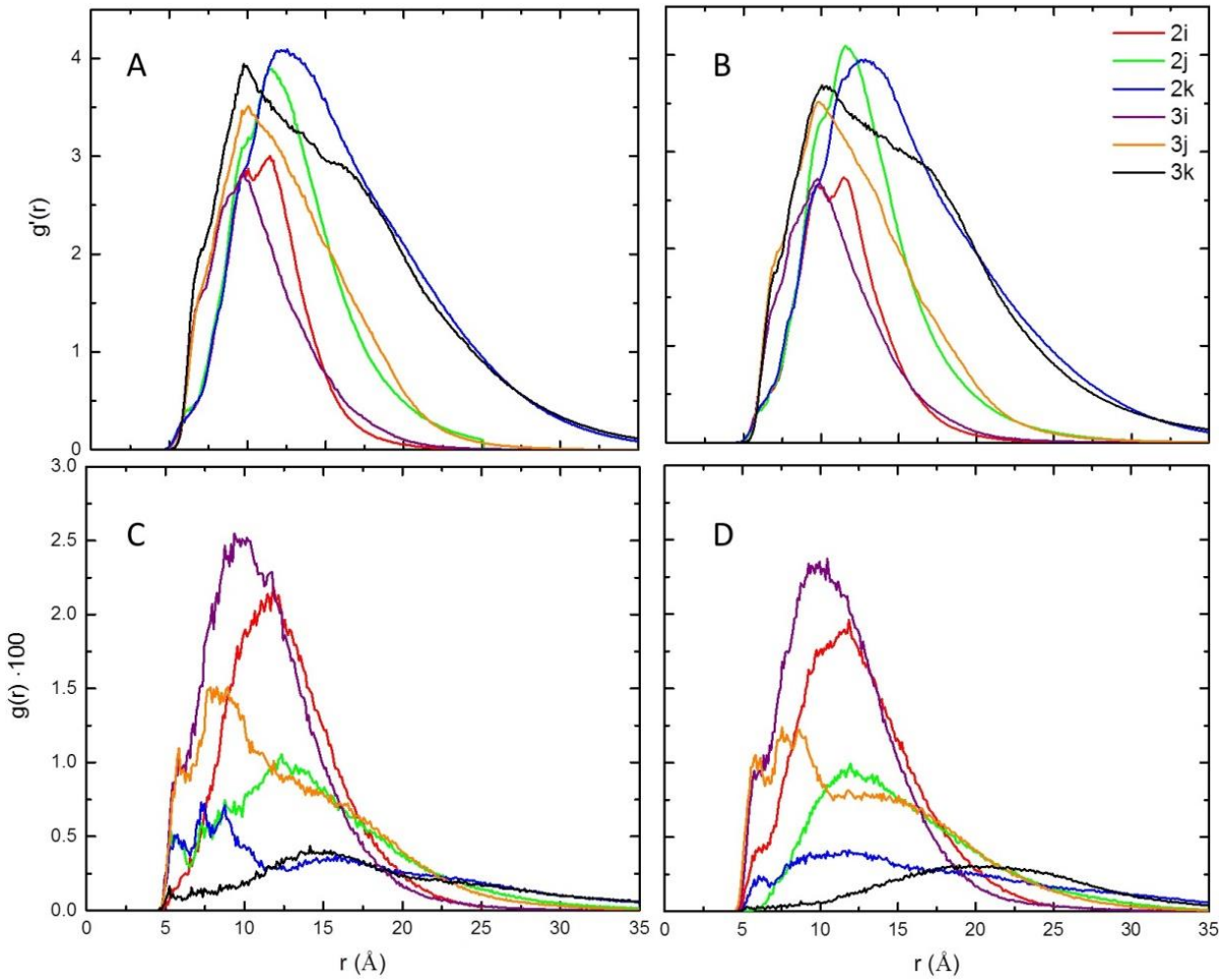


Supplementary Figure 2. Nanoparticles snapshots in 0.08 M buffer solution at pH=7.4 (salt) after 31 ns of simulations. Scale bar is 1 nm. A) **2i** B) **3i** C) **2j** D) **3j** E) **2k** F) **3k**.

We use the simulated trajectories of the NPs to calculate the radial distribution functions (RDF), g(r), from Eqn. 1. It gives the relative probability of finding the j^{th} atom at a distance r from the i^{th} atom with respect to the bulk density:

$$g(r) = \frac{1}{V\rho_N}\sum \delta(r - r_{ij}) \; . \qquad (1)$$

In Eqn. 1, δ is a delta function, r_{ij} is the distance of i^{th} and j^{th} atoms, and V is a volume, $\int 4\pi r^2 dr$, used in a normalization, and ρ_N is the number density of the used species (the number of atoms N_O used in Eqn. 1 divided by the volume of the simulation box). We use Eqn. 1 when we analyze the distribution of C terminal atoms, which are fixed for a given number of ligands (12). When, we consider the distribution of all PEG-chain oxygens (varying number), we remove N_O (equal the total number of PEG chain oxygens) from ρ_N, by multiplying Eqn.1 by N_o, to get $g'(r)$, where we account for the growing distributions for longer PEG chains (more oxygens; system volume is fixed).



Supplementary Figure 3. RDFs of **2i–k** and **3i–k** NPs. g'(r) calculated for A) boron-PEG oxygen atoms in water and B) boron-PEG oxygen atoms in ionic solution. g(r) calculated for C) boron-terminal C atoms in water and D) boron-terminal C atoms in ionic solutions.

In Supplementary Figure 3, we have calculated g'(r) for (A, B) all the oxygens in PEGylated chains and g(r) for (C, D) terminal carbon atoms of the PEGylated chains. All the cases were calculated with respect to all the boron atoms. We can clearly see that as the chain becomes longer, the oxygen (A, B) distributions become wider and their peaks, r_{max}, become slightly shifted to higher values. Steric effects prevent longer PEGylated chains from folding and wrapping close to the B core, therefore, preventing them from significantly affecting r_{max}. The systems present in

water and ionic solutions have almost the same PEG-oxygens distributions. On the contrary, in the terminal carbon (CD) distributions, the peaks maxima, r_{max}, are significantly shifted to higher values with the chain lengths, since the terminal C atoms are further away from the NPs cores, which they cannot reach. In these distributions, we can also see some differences between water and ionic solution cases, revealing that the terminal atoms in long PEGylated chains are slightly more outstretched in ionic solutions.

The $g^{'}(r)$ distributions (Supplementary Figure 3 A, B) are similar for the **2** and **3** types of ligands, except of some deformations present in the **3** types. These deformations slightly shift the **3** type peaks (r_{max}) to smaller values. For all but **2k** and **3k** terminal carbon RDFs, **3** type ligands have consistently smaller r_{max} values than their **2** type counterparts (Supplementary Figure 3), even though **3** has an extra aromatic group, slightly increasing the maximum possible ligand length. The extra aromatic group in **3** ligands enhances π-π stacking interactions between the ligands, thus causing the net length to decrease. The split peak in **2i** could be related to the fact that the B shell front and back sides can contribute by separate peaks.

The hydrodynamic radii of the studied NPs were estimated from the regions of decaying $g^{'}(r)$ (half value compared to r_{max}) for the cases (A–B) (all oxygens). In water, the hydrodynamic radii of **2i** and **3i** are 12 Å; **2j** and **3j** are 15 Å; **2k** and **3k** are 20 Å. In the ionic solution, **2i**, **3i**, **2j**, and **3j** have very similar sizes as in water. At certain times, there are some chains on **2k** or **3k** that extend outwards, but most of the other chains are folded (Supplementary Figures 1 E, F and 2 E, F). Interestingly, the maxima of distributions for the terminal C atoms in Supplementary Figure 3 C, D match relatively well to the hydrodynamic radii. One can assume that the terminal C atoms are distributed at the surface of the NPs, revealing thus their radii.

To confirm the previous results, next, the radii of gyration, $\langle r_{gyr} \rangle$, are also calculated for NPs using Eqn. 2:

$$r_{gyr} = \sqrt{\frac{I}{m}} = \sqrt{\frac{\sum_{i=atoms} m_i(\vec{r}_i - \vec{r}_{com})^2}{\sum_{i=atoms} m_i}} \quad . \quad (2)$$

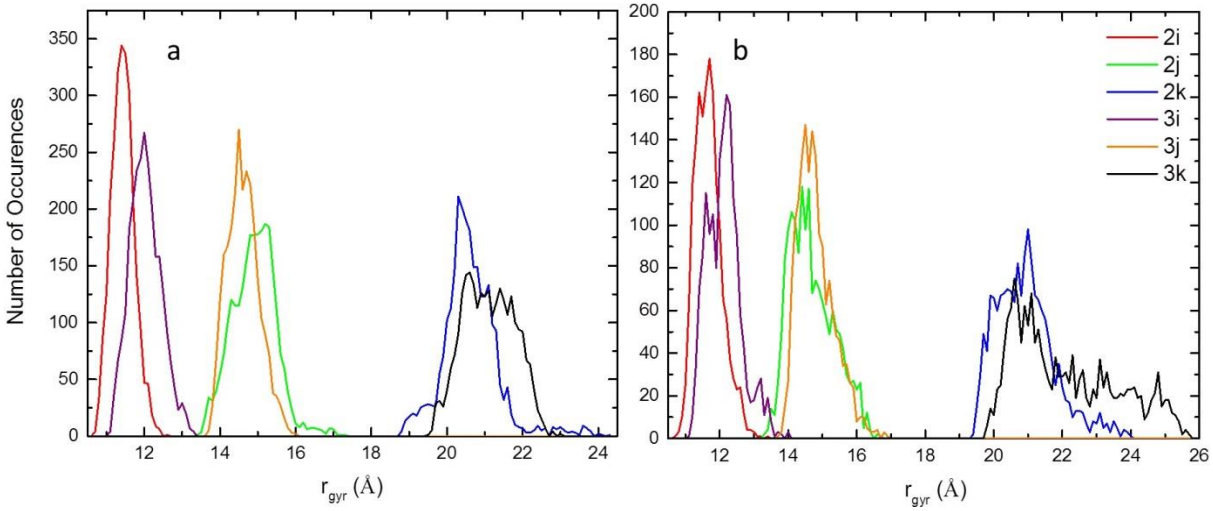
Here, I is the moment of inertia of the molecule, m is the total mass of the molecule formed by individual contributions, m_i, of atoms shifted with respect to a molecular center of mass, r_i-r_{com}. Time averaged $\langle r_{gyr} \rangle$ was calculated by using equation 2 every 10 ps over 26 ns trajectory (water) or 34 ns trajectory (salt solution) and then averaged. Standard deviations and confidence intervals were also computed.

Supplementary Table 2. Radii of gyration, $\langle r_{gyr} \rangle$, and their confidence intervals for PEGylated species in water and salt solutions.

Molecule	Solvent	$\langle r_{gyr} \rangle$ (Å)
2i	water	11.5 ± 0.9
2j	water	15.0 ± 1.7
2k	water	20.7 ± 2.2
3i	water	12.1 ± 1.2
3j	water	14.7 ± 1.3
3k	water	21.1 ± 2.0
2i	ionic solution	11.7 ± 1.0
2j	ionic solution	14.7 ± 2.0
2k	ionic solution	21.0 ± 2.5
3i	ionic solution	12.2 ± 1.5
3j	ionic solution	14.8 ± 1.6
3k	ionic solution	22.1 ± 4.5

Supplementary Table 2 shows the radii of gyration, $\langle r_{gyr} \rangle$ and their >99.5 % confidence intervals for PEGylated species in water and salt solutions. As expected, **2i** and **3i** molecules have the smallest diameters, whereas **2k** and **3k** have the largest diameters in both environments. **2i** and **3i**

molecules, with 7 PEGylated oxygens per ligand have diameters of more than 2 nm; **2j** and **3j**, with 16 PEGylated oxygens per ligand, less than 3 nm; **2k** and **3k**, with 43 oxygens per ligand, more than 4 nm. NPs with the type **3** ligands tend to have a slightly larger diameter than those with the type **2** ligands. This size increase could be due to the extra aromatic group in type **3** ligands, which is absent in the **2** type ligands. $\langle r_{gyr} \rangle$ does not change appreciably between the two environments. However, **2k** and **3k** ligands are slightly more outstretched in the ionic solutions.



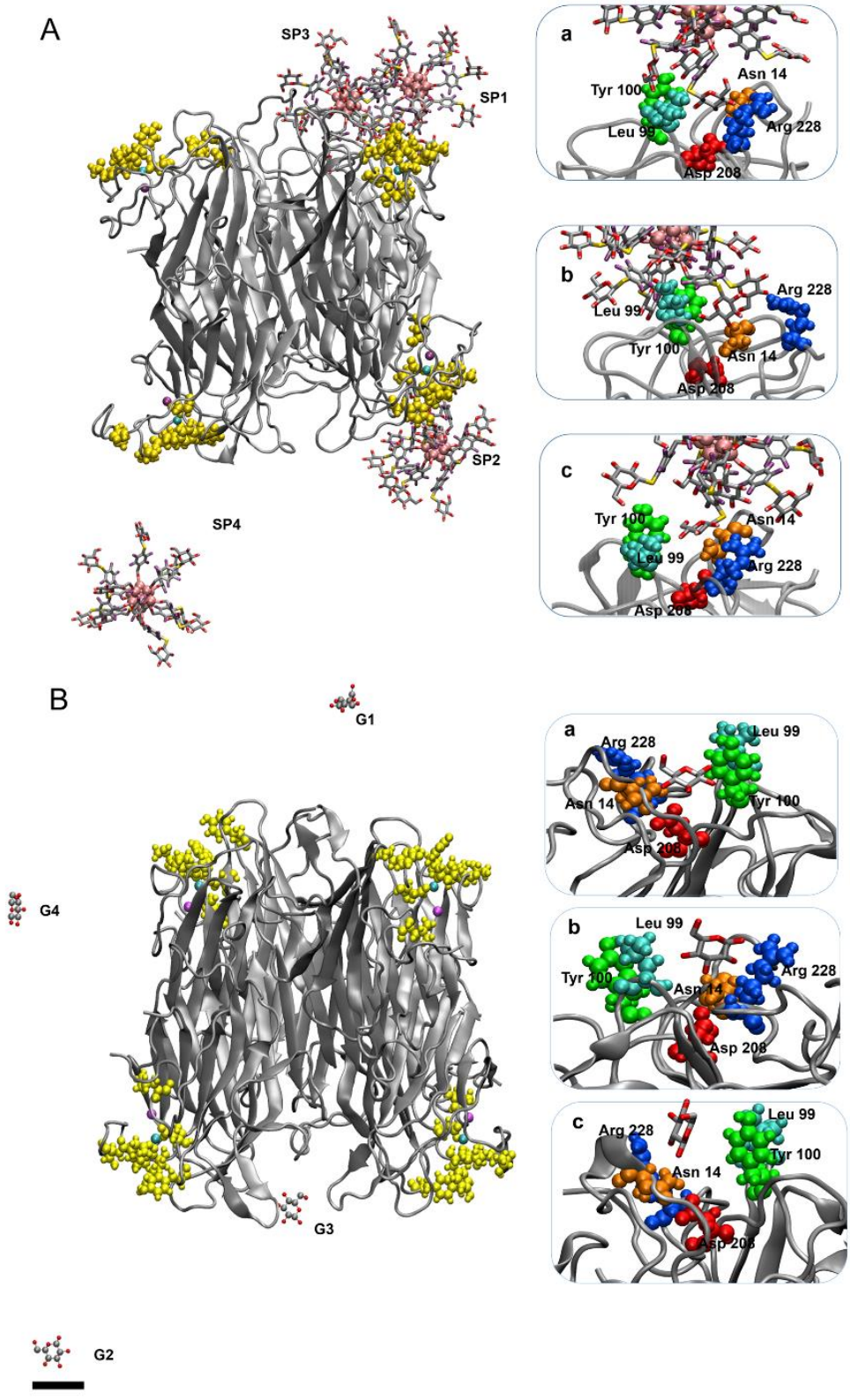
Supplementary Figure 4. Distributions of r_{gyr} in a) water and b) ionic solutions.

Supplementary Figures 4a and b show the distributions of r_{gyr} in water and salt solutions, respectively. The distributions are asymmetrically broadened at higher values for all molecules, especially for long chains. This reflects that a few chains could extend and then fold back. Comparing the radii of gyration, $\langle r_{gyr} \rangle$, from Supplementary Table 2 and Supplementary Figure 4 with the above hydrodynamic radii and the most likely positions of terminal C atoms, we can see that all these parameters are in good agreement.

B. Sugar-coated nanoparticles – protein binding

MD simulations were also performed to investigate multivalent binding of sugar-coated nanoparticles and proteins. Concanavalin A (Con A) was chosen as the target protein to bind with

multivalent sugar-coated particles (SP) and monovalent β-D glucose (G), respectively. Con A forms quaternary structures, giving at pH 7 a tetramer, having four carbohydrates binding sites (hydrogen bonds)[21]. In each Con A, up to 15 amino acids can be involved in the carbohydrate binding, while for the monosaccharide binding only five amino acids are involved, including Asn 14, Leu 99, Tyr 100, Asp 208, Arg 228[22]. In our simulations, the tetramer structure of Con A used was based on X-ray diffraction data (PDB code 1ONA)[22]. Supplementary Figures 5A and B show the structures of tetramer of Con A with SPs and β-D glucose after 20 ns simulation. The metals manganese (magenta ball) and calcium (cyan ball) were added in Con A according to its metal binding sites[22]. The monosaccharide binding sites are distinguished from the backbone of Con A by different colors (shown in Supplementary Figure 5). The Con A tetramer has four binding positions. We name the top right position as binding position 1 (B1), bottom right as B2, top left as B3, and bottom left as B4.



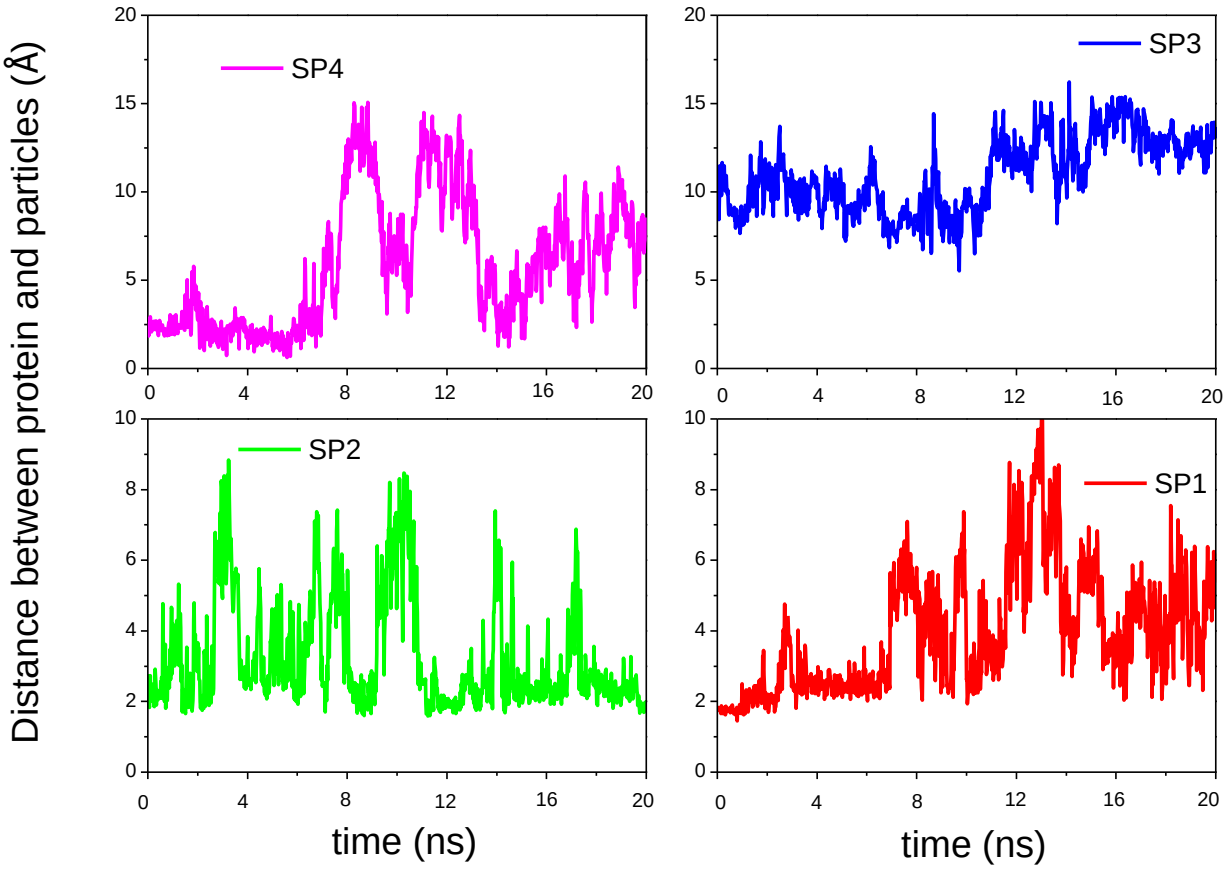
Supplementary Figure 5. A) Tetramer of Con A and sugar-coated particles. B) Tetramer of Con A and β-D glucoses. Details of glucose binding shown in both cases.

For the NPs binding, three SPs (SP1, SP2 and SP4) were initially put near the binding sites of chosen monomers. The last SP (SP3) was placed in the cavity between the B1 and B3 binding positions. For the β-D glucose binding, three glucose molecules (G1, G2 and G3) are separately placed at the binding B1, B2 and B3 positions, while the last glucose molecule (G4) was placed between the B3 and B4 binding position. The two systems were immersed in water together with the counter-ions and the simulations were performed with NAMD[10].

The bond, angle and dihedral parameters of protein, SPs (nanoparticle **2l** in Table 2) and β-D glucose were implemented from the CHARMM[11–16] force field. The parameters for the boron core and ligands were used the same as in the PEGylated calculations. The nonbonding parameters of Mn^{2+} ions were based on the calculations of Babu *et al*.[23]. Nonbonding interactions of SPs were calculated using a cut-off distance of 10 Å, whereas long-range electrostatic interactions were calculated by the PME method[20] in the presence of periodic boundary conditions. The systems were simulated in the NPT ensemble, using a Langevin dynamics with a damping constant of 0.01 ps^{-1} and a time step of 1 fs.

First, we modeled the coupling between SPs and the Con A tetramer. At each simulation time, we have calculated a distance between each sugar binding site and its nearest ligand in the SP. Supplementary Figure 6 shows a time-dependent distance between the nearest SPs ligand and the Con A tetramer. During the 20 ns simulations, SP1 and SP2 have an average distance of 4 Å, while SP3 and SP4 have an average distance of about 10 Å. Because the initial position of SP3 is far from any binding site, it can't bind during the short simulations. From Supplementary Figure 5A, we can see that SP3 competes with SP1 for the B1 position, while SP4 shows a different trend. Within 1 ns, SP4 comes near to the Con A tetramer and binds to it. Then, it leaves away and binds

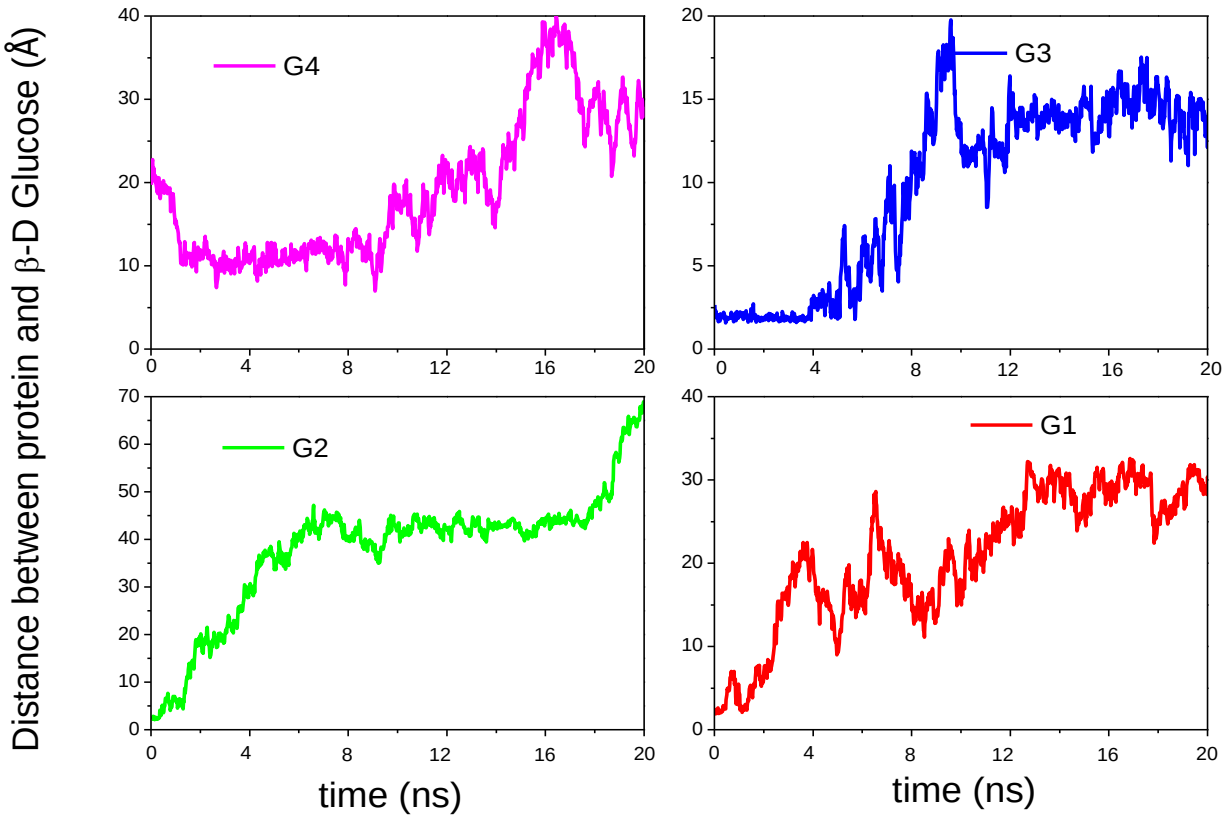
again at 4 ns, when the binding lasts for about 4 ns. After 12 ns, SP4 binds to the Con A tetramer again.



Supplementary Figure 6. Nearest distances between SPs ligands and the Con A tetramer.

Supplementary Figure 6 reveals that when SPs bind to the Con A tetramer their binding distance is about 1.8-2 Å. SPs occasionally gain and preserve for significant time periods these small binding distances. Supplementary Figure 5 A(a-c) show details of SP1, SP2 and SP4 binding to their binding sites. We can see that in all the cases only one of the SPs ligands binds to the nearby binding site, composed of Asn 14, Leu 99, Tyr 100, Asp 208, Arg 228, which is the monosaccharide binding site shown in different color in Supplementary Figure 5 A(a-c). Therefore, there is always one ligand of SPs which performs like a monosaccharide when binding to the Con A tetramer. Because the SPs have several ligands, when one ligand leaves, another

nearby ligand comes and binds, which increases the binding probability of SPs. In this way, SPs act like multivalent binders.



Supplementary Figure 7. Nearest distances between β-D glucose molecules and the Con A tetramer.

In order to compare the binding ability of SPs and β-D glucose systems, we simulated binding of β-D glucose and the Con A tetramer. Supplementary Figure 7 shows the nearest distance between β-D glucose and Con A as a function of time. Supplementary Figure 7 shows that G1 only binds to Con A at the first 1 ns and then leaves. G2 only binds at the very beginning and it doesn't bind later; G3 binds to Con A for about 4 ns at the beginning and after that it leaves away; G4 shows weak binding during the first 4 ns. The average distance between all the β-D glucose molecules and the Con A tetramer is more than 20 Å, except G3 whose average distance is about 12 Å. Supplementary Figure 5B(a-c) shows details of β-D glucose and the Con A tetramer binding.

When β-D glucose binds to Con A, it binds to the typical monosaccharide binding sites. Because β-D glucose is monovalent, when one β-D glucose leaves, another β-D glucose from the surrounding solution might come nearby and bind. Overall, monovalent β-D glucose molecules show shorter binding times and longer binding distances than SPs.

References

1. Safina, G., Duran, I. B., Alasel, M. & Danielsson, B. Surface plasmon resonance for real-time study of lectin–carbohydrate interactions for the differentiation and identification of glycoproteins. *Talanta* **84,** 1284–1290 (2011).
2. Sheldrick, G. M. SHELXT – integrated space-group and crystal-structure determination. *Acta Cryst.* **A71,** 3–8 (2015).
3. Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* **A64,** 112–122 (2008).
4. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2 : a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42,** 339–341 (2009).
5. Wixtrom, A. I. *et al.* Rapid synthesis of redox-active dodecaborane $B_{12}(OR)_{12}$ clusters under ambient conditions. *Inorg. Chem. Front.* **3,** 711–717 (2016).
6. Messina, M. S. *et al.* Visible-light-induced olefin activation using 3D aromatic boron-rich cluster photooxidants. *J. Am. Chem. Soc.* **138,** 6952–6955 (2016).
7. Becer, C. R. *et al.* Clicking pentafluorostyrene copolymers: synthesis, nanoprecipitation, and glycosylation. *Macromolecules* **42,** 2387 – 2394 (2009).
8. Hood, C. A. *et al.* Fast conventional Fmoc solid-phase peptide synthesis with HCTU. *J. Pept. Sci.* **14**, 97-101 (2008).
9. Zou, Y. *et al.* Convergent diversity-oriented side-chain macrocyclization scan for unprotected polypeptides. *Org. Biomol. Chem.* **12,** 566–573 (2014).
10. Phillips, J. C. *et al.* Scalable molecular dynamics with NAMD. *J. Comput. Chem.* **26,** 1781–1802 (2005).

11. MacKerell, A. D. *et al.* All-atom empirical potential for molecular modeling and dynamics studies of proteins. *J. Phys. Chem. B* **102,** 3586–616 (1998).
12. Vanommeslaeghe, K. & MacKerell, A. D. Automation of the CHARMM general force field (CGenFF) I: bond perception and atom typing. *J. Chem. Inf. Model.* **52,** 3144–3154 (2012).
13. Vanommeslaeghe, K., Raman, E. P. & MacKerell, A. D. Automation of the CHARMM general force field (CGenFF) II: assignment of bonded parameters and partial atomic charges. *J. Chem. Inf. Model.* **52,** 3155–3168 (2012).
14. Yu, W., He, X., Vanommeslaeghe, K. & MacKerell, A. D. Extension of the CHARMM general force field to sulfonyl-containing compounds and its utility in biomolecular simulations. *J. Comput. Chem.* **33,** 2451–2468 (2012).
15. Mackerell, A. D., Feig, M. & Brooks, C. L. Extending the treatment of backbone energetics in protein force fields: limitations of gas-phase quantum mechanics in reproducing protein conformational distributions in molecular dynamics simulations. *J. Comput. Chem.* **25,** 1400–1415 (2004).
16. Vanommeslaeghe, K. *et al.* CHARMM general force field: a force field for drug-like molecules compatible with the CHARMM all-atom additive biological force fields. *J. Comput. Chem.* **31,** 671–690 (2010).
17. Gaussian 09, Revision D.01, Frisch, M. J. *et al.* Gaussian, Inc., Wallingford, CT (2013).
18. Breneman, C. M. & Wiberg, K. B. Determining atom-centered monopoles from molecular electrostatic potentials. The need for high sampling density in formamide conformational analysis. *J. Comput. Chem.* **11,** 361–373 (1990).
19. Mayne, C. G., Saam, J., Schulten, K., Tajkhorshid, E. & Gumbart, J. C. Rapid parameterization of small molecules using the force field toolkit. *J. Comput. Chem.* **34,** 2757–2770 (2013).

20. Darden, T., York, D. & Pedersen, L. Particle mesh Ewald: an N·log(N) method for Ewald sums in large systems. *J. Chem. Phys.* **98,** 10089–10092 (1993).
21. Loris, R., Hamelryck, T., Bouckaert, J. & Wyns, L. Legume lectin structure. *Biochim. Biophys. Acta - Protein Struct. Mol. Enzymol.* **1383,** 9–36 (1998).
22. Loris, R., Maes, D., Poortmans, F., Wyns, L. & Bouckaert, J. A structure of the complex between Concanavalin A and methyl-3,6-di-O-(α-D-mannopyranosyl)-α-D-mannopyranoside reveals two binding modes. *J. Biol. Chem.* **271,** 30614–30618 (1996).
23. Babu, C. S. & Lim, C. Empirical force fields for biologically active divalent metal cations in water. *J. Phys. Chem. A* **110,** 691–699 (2006).